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Sorption Processes in Nanofibers

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Abstract

With the increasing concern of colour removal from wastewater before discharging it to the environmental rivers and with the knowledge of sorption process as being the only process so far which can remove dyes effectively on wastewater, however the current sorbent materials used in this process are expensive. This yield attention in finding cheaper sorbent material that would be able to solve the current latter. Recently there has been much attention paid to nanofibers as alternative sorbents because of the high surface area they propound. In this study electrospun polyamide 6 nanofibers were used as the sorbent material to remove colour of dyes in the simulated wastewater concentration of textile industries, using sorption-filtration method which was able to remove dye in relatively short time since the system was under vacuum pressure and the sorbent thickness by adding more nanofiber layers was tested, where it was concluded that the percentage of dye removal increases if the thickness (more nanofiber layers) of sorbent was increased. The presented process has more potential in dye removal studies because the sorbent (nanofilter) was protected from mechanical damage and it possible to perform many experiments in short time.

The sorption properties of nanofibers were also tested by kinetics experiments and equilibrium experiments where two substrate of polyamide 6 (standard fibres and nanofibers) were compared in both experiments. The Cegarra-Punte was the best fit theoretical model to describe kinetics experiments, where Langmuir isotherm was the best model for describing equilibrium experiments. With Langmuir saturation constant S it was concluded based on the obtained result that nanofibers had 10 time higher saturation value when compared to standard fibres which was explained by the high surface area that nanofibers offer. The diffusion coefficient was also used to further study the sorption properties of the two substrates.

List of abbreviations

1) S = Langmuir saturation constant
2) K = Langmuir rate constant or rate constant
3) Ce = equilibrium concentration
4) t = time
5) At = absorbency after sorption process of liquor
6) Ao = absorbency before sorption process of liquor
7) C.I = colour index number
8) CL = concentration of liquor after sorption
9) CLo = concentration of liquor before sorption
10) Cs = concentration of dye in substrate
11) g/L = grams per litre
12) mg/g = milligrams of dye in fibre per gram of fibre
13) mD = mass of dye in fibre
14) mF = mass of fibre
15) A = area of substrate
16) PA = Polyamide 6
17) $t_{1/2}$ = half time of dyeing

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1 Introduction

The extensive use of dyes in textiles, printing, dyeing, and food plants has produced a large amount of dyes in their wastewater. Because some dyes and their degradation product may be carcinogen and toxic, the removal of dyes from wastewater becomes a vital issue in environmental protection [21, 22, and 23]. Furthermore the presence of unfixed dyes in textile industry is perceived as one of the major environmental problems of textile wastewater, because colour is visible to the public even if the concentration of dye is lower than other pollutants, which increases the need for it to be removed before it is discharged [23].

The treatment of dye effluent is rather not easy because of their synthetic origins and their mainly aromatic structure, which are biologically non degradable. This prevails on intensive search for the best available technology for the dye removal. Various physio-chemical methods have been put forward to satisfy the above requirement (such as advanced oxidation, biological process, coagulants, oxidizing agents, membrane, electrochemical, and sorption techniques). Amongst all these chemical and physical methods sorption process is one of the effective techniques that so far have been successfully employed for colour removal. [21, 23, 24] In this process various adsorbents (sorbents) have been examined to reduce dye concentrations from aqueous solutions. Activated carbon is regarded as an effective one however expensive adsorbent due to its high cost of manufacturing and generation, some others including peat, chitin, silica and some agriculture waste has also been utilized but sorption capacities of the above adsorbent are not very high. To improve efficiency of sorption process, it is necessary to develop cheap and easily available adsorbents with high sorption capacities [24].

Since extraction mainly relies on the holes of the surface of material and limited active groups ,this means chemical composition and morphology characteristic of the sorbent are the limits for the efficiency and sorption capacity, while available or currently used sorbents are normally micrometer-sized[25,18]. With this increasing demand on finding the best suitable sorbent, more attention has been paid to nanostructure materials represented by

nanofibers. The high surface –to- volume ratio of nanostructure materials provides the numerous deal of active site for sorption, making a foundation for efficient separation, extraction and enrichment. [25] Furthermore there has been a great interest on research and development of nanofibers in recent years due to the heightening awareness of it potential in medical and engineering applications. [16] The widely accepted technique to fabricate submicron polymer fibers to engineer unique functional nanostructure is electrospinning. [17,18]. The electrospining process is a fiber forming process, where high voltage is used to create an electrically charged jet of polymer solution or melt from the needle [17]. Nanofibers have a strong penetrability and interaction with other compounds, which make sorption more superior, and due to their high porosities and interconnected pore structure offer a high permeability to water filtration over conventional used materials.[16,25,28] When nanofibers are compared to macro scale adsorbents electrospun nanofibers own a high surface-to-volume ration and length to the diameter ration that can provide a larger specific surface and more active sites for sorption: accordingly the attachment of the target molecules would facilitate and a small amount of nanofibers is adequate for the extraction, which greatly reduces the volume of desorption solvent. [27]

In this study polyamide 6 electrospun nanofibers were used as sorbent material to study the sorption-filtration process of simulated solution of dye wastewater. Four acid dyes were chosen as the target sorbate on the simulated wastewater for textile industry due to their high affinity to polyamides. Important parameters were calculated which define the capability of substrate.

Also the sorption properties were further studied by conducting kinetics experiments and equilibrium experiment, where the sorption properties of standard fibres were compared to the sorption properties of nanofibers. Kinetic models were used to describe the kinetics experimental result obtained and equilibrium isotherms used for modelling equilibrium experimental result.

2 Theoretical part

2.1 Back ground about nanotechnology and nanofibers

Since nanofibers falls under the umbrella termed nanotechnology it is best to fist define what nanotechnology is. Nanotechnology is an emerging interdisciplinary area expected to have wide ranging implications in all fields of science and technology such as material science, mechanics, electronics, optics, medicine, energy, and aerospace, plastics and textiles. To define nanotechnology the word 'nano' in this technology stands for one billionth of a meter, i.e. 1 nm = 10^{-9} m. Nano comes from the Greek word for 'dwaf' and approximately 10 000 times finer than human hair. The National Nanotechnology Initiative (NNI) defines nanotechnology as the utilization of structure with at least one 'nano' dimension for the construction of materials, device or systems with novel or significantly improves properties due to their 'nano' size [1, 2].

This technology does not only produce small structures but is also an anticipated manufacturing technology, which can give thorough inexpensive control on the structure of matter. The fundamental of nanotechnology lies in the fact that properties of materials change dramatically when their size is reduced to the nanometer range. The origin of this technology is sad to be not new as Mother Nature perfected it millions of years ago. This is based on the self-cleaning properties of lotus leaf, which are due to its carefully designed nanostructured surface and tooth and bone are natural nano biocomposites being excellent example of nanotechnology already existing in nature. However, the embryo of nanotechnology is believed to be the concept of 'atomic assembly' which was openly articulated in 1959 by Nobel Laureate and physicist Sir Richard Feynman, in his famous lecture titled 'there is plenty of room at the bottom'. Though he never explicitly mentioned "nanotechnology" Feynman suggested that it will eventually be possible to precisely manipulate atoms and molecules. The term 'nanotechnology' was first coined by Norio Taniguchi at University of Tokyo in 1974, when he defined the theoretical dimensions and tolerances in technology and also described the precision manufacturing of materials with nanometer tolerances. With the background of 'nano'and nanotechnology it is therefore

necessary to define the term fiber so as to fully define the term nanofibers. The word fiber from the textile industry point of view it is a natural or synthetic filament, such as cotton or nylon, capable of being spun into yarn, or simply as material of such filaments.

2.1.1 Full description of nanofibers

Definition of nanofiber is a nanomaterial in view of its diameter, and can be considered a nanostructure material if filled with nanoparticles to form composite nanofibers, and nonwoven industry generally considers nanofibers as having a diameter of less than one micron, where the National Science Foundation (NSF) defines nanofibers as having at least one dimension of 100 nanometer (nm) or less.

2.1.2 Traditional production of fibers and current process of producing nanofibers

The conventional fiber spinning techniques such as wet spinning, dry spinning, melt spinning and gel spinning usually produce polymer fibers with diameters down to the micrometer range. When the fiber diameter is reduced from micrometers to nanometers, very large surface area to volume ration are obtained and flexibility in surface functionalities and better mechanical performance may be achieved. The process of producing nanofibers is electrospinning process; it has received a great deal of attention in the past decade because of its ability to consistently generate polymer fibers that range from 5 to 500nm in diameter [1, 11, and 13].

2.1.3 Electrospinning process

History about electrospinning dates back to more than 60 years. Formhals introduced electrospinning methods and described fiber formation during spinning process [2, 3]. This process is regarded as a simple and versatile method to produce ‘nano’ to sub micrometer fibers. The resulting nanofibers from electrospinning offer a unique advantage as they have high specific area, good interconnectivity of pores and the possibility to incorporate active components on a nanoscale which makes these fibers the best candidates in many applications such as filtration, manufacture of protective clothing, pharmaceuticals and tissue engineering

2.1.4 How fibers are formed in electrospinning

In electrospinning process, the viscous solution of polymer is sprayed through the syringe spinneret, a Taylor cone is formed at the tip of the pendant droplets. This is due to the high electrostatic forces between the tip and the collector. Above the critical voltage, electrostatic forces overcome the surface tension of this electrospinning solution and an electrified polymer jet is formed. Under these conditions the jet is elongated and whipped continuously by electrostatic repulsion until there is deposition on the grounded collector.

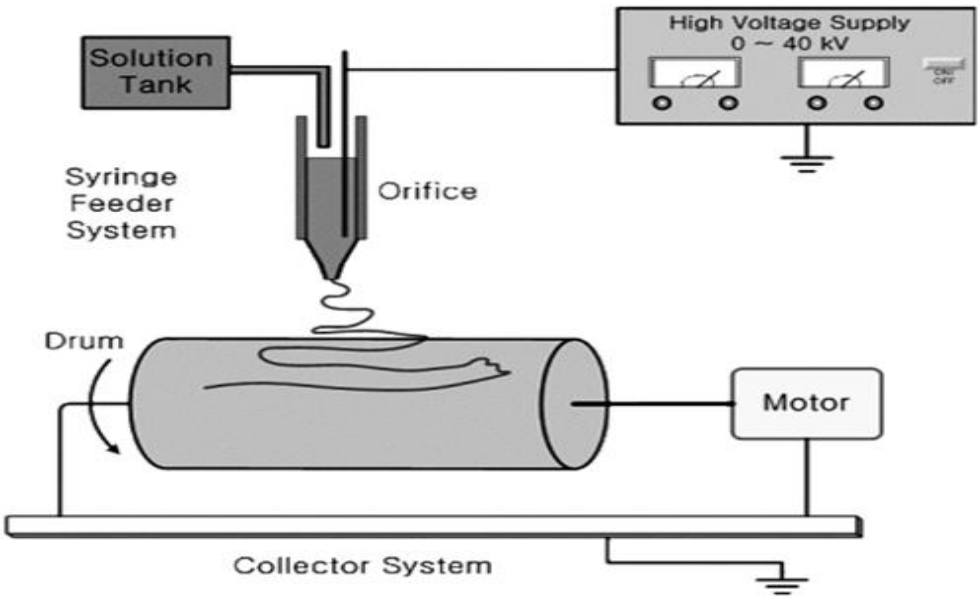


Diagram 1: Illustration of the electrospinning apparatus [14]

2.1.5 Factors that affect the formation of fibers in electrospinning

Several factors that can influence the formation of fibers from polymer solution through electrospinning have been examined by to general approaches: examining the effects of material/ process parameters and development of new functionalities. These parameters are intrinsic properties of the solution such as conductivity, surface tension, viscosity, polymer molecular weight and concentration, and operational conditions such as applied voltage, temperature, humidity, solution flow rate, nozzle diameter, spinneret-collector distance and motion of the collector.

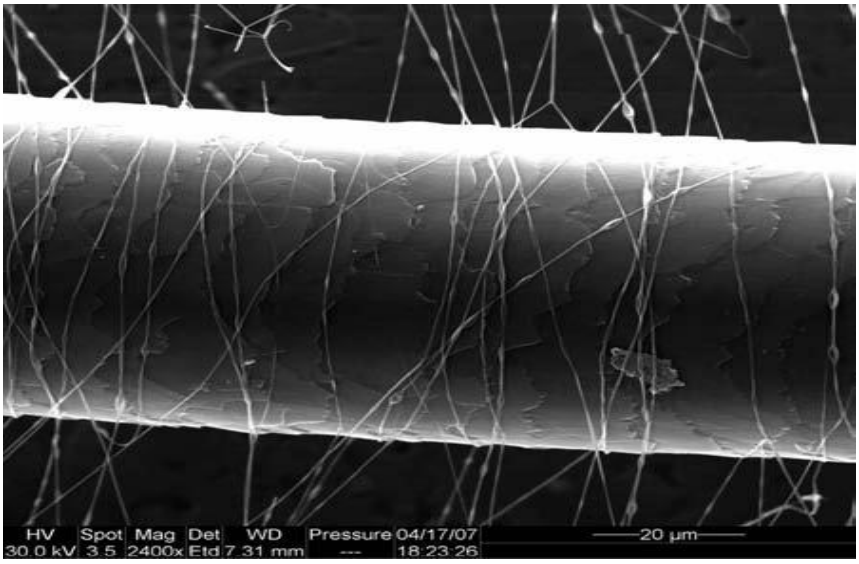


Diagram 2: SEM image comparing the diameter of a human hair with that of PMMA nanofibers electrospun from DMF solution. (Courtesy of RTI International.) . It can be observed that there is a big difference in terms of size.[12]

2.1.6 Practical application

The nonbiomedical application of electrospun nanofibers is filtration which already has products in the market containing layers of nanofibers. It is also one of the areas where nanofibers are likely to make a significant and lasting impact. Another emerging application area for nanofibers is in sensors for sense chemical and biological agents including the growing number of toxic industrial chemicals.

2.1.7 The future of nanofibers

Impending advancements in nanofiber technology will be fuelled primarily by improvements in electrospinning technology and process control to allow consistent production of nanofiber mats with single-digit fiber diameters, and the potential to combine several physical, chemical, and biological functionalities into a single fiber to make multipurpose fiber mats and smart materials a reality. The functionalities considered need to move well beyond the simple passive effects of biocidal effectiveness (for instance by incorporating nanosilver), super hydrophobicity by surface texturing, or simple breathable biodegradable wound dressings. Future nanofibers are likely to deliver far more advanced

multiple functionalities and will likely be active devices that perhaps enable impressive disruptive technologies. These will include fabric-based computing/communications capabilities (integration of circuitry and transponders into nanofibers), the enabling base technologies for all these are already on the horizon as far as material choices go, but design, integration, and productization has yet to be carried out. Refinements in electrospinning technology that will support these innovations broadly fall into two categories: innovations in process/materials and the recognition of new cross-disciplinary applications for electrospun materials [12].

2.1.8 Porosity and pore size distribution in nanofiber as to predicting the network.

It was discovered in mass distribution in random network can be expressed in terms of the dimensions of the fibre, and the coverage of the network and that while this distribution of mass is not influenced by the mean porosity of the network, other properties, such as the number of crossing between fibre and the available fraction of the fibrous surface area, are [13]

There has also been some computation that the mean pore radius for a range of fiber morphologies and network properties that are likely to be appropriate to the study of nanofibrous assemblies. Thus there was consideration of fibres of circular cross-section, with diameter up to 100 nm. The assumption of a circular cross-section permits a unique and simple relationship between diameter and linear density, which is influenced only by the density of the material from which the fibre are formed. We have assumed fibre densities between 0.9 and 1.7 g cm^{-3} to include values quoted in the literature for polycaprolactone, carbon nanotubes and cellulose fibre. This range of values also includes most forms of polymeric materials currently used in electrospinning. The porosity range of interest here is between 0.7 and 0.9, as previously discussed. The final parameter influencing the pore radius distribution is the mean areal density of the network. Not much literature that reports these properties of nanofibrious network, some study suggests a value of about 20 g m^{-2}, and as such this can be used as an upper limit for calculations. The result observed the mean pore size increases with increasing porosity, and decreases with increasing areal density and decreasing fiber density since these parameters influence the total fibre length per unit area

in the network, and hence increases the total length of void perimeter. The conclusion reveals that mean pore radius may be more important to define the electrospun substrates not porosity [13].

2.2 Nylon (Polyamide) background

Nylon was the first commercialized synthetic fiber and is used throughout the world in many applications i.e. it has been widely used as an important engineering plastic and synthetic fiber because of it good mechanical properties [4]. Under nylon there are various types of nylon but in this presented work Nylon 6 (polyamide 6) was used in the form of nanofibers and also as standard fiber. Polyamide 6 is a biodegradable, biocompatible and synthetic polymeric material having good mechanical properties. Traditionally they were produced by methods such as melt, wet and dry spinning and is available in staple, tow, monofilament and multifilament [4]. However fibers produces by these methods range from 10 to 500 μm and if polyamide 6 fibres are manufactured into nano to micro sized nonwovens it would be able to further expand its applications in speciality material.

2.2.1 Properties of standard polyamide 6 fibres

2.2.1.1 Mechanical properties

- Tensile strength : 3.6 – 7.5 cN/dtex
- Elasticity :23-25 %
- electric recovery : 10^{11} ohms m
- elasticity modulus : 340 cN/tex
- density crystalline structure :1170 kg/m^3
- density for amorphous structure : 1084 kg/m^2
- degree of polymerization : 100 - 200

2.2.1.2 Thermal and thermomechanical properties

- Glass temperature [Tg] : 40-80 degrees depending on the instrument used
- Softening temperature : 170^{o}C
- Melting temperature : 225^{o}C
- LOI (Limited Oxygen Index) : 0.201
- Thermal conductivity : 0.245- 0.3 W/mK
- Heat capacity : 1.592- 1.7 J/kg.K
- Moisture absorption : 9-12 % from dry sample [5]

2.2.1.3 Electrical properties

- Low friction coefficient
- Good electrical insulator

2.2.2 Chemical stability of polyamide 6

Polyamide is less resistant to acids than it is to alkalis. Prolonged and frequent exposure to alkalis will cause significant alkali hydrolysis of polyamide polymers. Since polyamide 6 textile material are inherently white and do not require bleaching, but in some extents when bleaching is necessary, the only bleaches than can be used under slightly alkaline conditions are oxidizing bleaches. Polyamide 6 has only a fair resistance to sunlight and weather, this is attributed to the ultraviolet rays of sunlight causing the amino groups of the amide groups to react with the oxygen in air.

2.2.2.1 Colour fastness of polyamide 6

The following classes of dyes are most frequently used to dye or print nylon textile materials Acid, Disperse and pre metalized dyes. But acid dyes will be illustrated more since it is the dyes used for experimental part of the thesis.

2.3 Acid dyes

The dye molecules of acid dye are sodium salt and will dissociate in an aqueous dye liquor to form the acid dye anion. The dye anion is negatively charged and is attracted to the cationic or positively charged groups in the polyamide polymer. The cationic sites are the terminal amino groups which have acquired a hydrogen cation from the acid in the dye liquor.

The wash-fastness of acid dye or printed polyamide textile materials is fair to good and depends on the specific acid dye. The strength of the bond between the dye molecules and the polyamide polymer varies with different dyes. If bond is relatively weak, alkaline detergents can cause colour to be removed from polyamide textile materials. The good light-fastness of acid dyed and printed polyamide textile materials is due in part to the acid resistance of the acid dye anion which will resist the slightly acidic conditions of the atmosphere. More importantly, the electron arrangement within the acid dye chromophores is reasonably resistant to the degrading effects of the sun's ultraviolet radiation. Under humid conditions the light-fastness of acid dye or printed textile materials may be detrimentally affected as the acid dye anion will react more readily with oxygen from the atmosphere causing degradation of the dye anion. And result in fading [6].

2.4 Sorption process

The sorption process will be described in two particular views in this study since it was observed in two different processes. (Alley 1993) defines sorption process as being the attraction of an aqueous species to the surface of a solid. The sorbing species is usually an organic compound which is called the sorbate and the solid media the sorbate is attracted to is known as the sorbent [15]. Where else the textile industry's view on sorption process is defined by dyeing process. The dyeing process is concerned with coloured organic compounds which are soluble in appropriate solvents(sorbate) and which are capable of becoming absorbed on to molecular 'surface' of textile substrates (sorbent) in a controllable manner, and of diffusing within these substrates[7,10] .

The underlying principle behind this attraction results from some form of bonding between the contaminant and sorption receptor sites on the sorbent. Under the sorption process there are two processes involved which are adsorption and absorption. To state the difference between the two is that adsorption is the attraction between the outer surface of solid (sorbent) with particles and contaminant, whereas absorption is the uptake of the contaminant into the physical structure of the solid [7, 10].

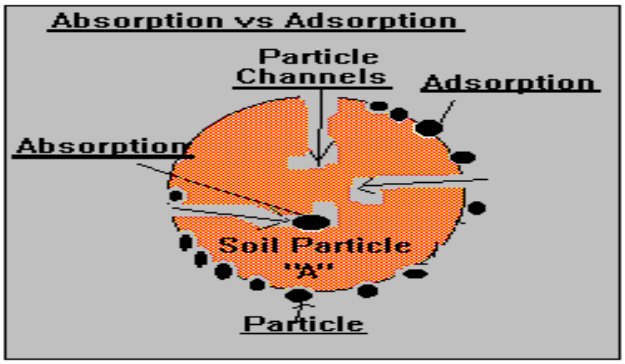


Figure.1: above illustrate the basic of the two processes [15]

The above figure illustration of the two processes of absorption and adsorption can be viewed as the basic principle of sorption in removal of wastewater contaminants and also in the dyeing of textiles. Adsorption from solutions onto solid surface is important in many industrial practices, such as dye or organic contaminant removal, edible oil clarification by

activated carbon, and ion exchange, where the adsorption of ions from electrolyte solutions is carried out. Adsorption from solution is a broad subject including detergents, dye, ion, polymer and biological material adsorption on solids, and huge amount of literature has been published in this field, since it is important to many industries [8, 7, 9, and 10].

2.4.1 Standard affinity of dye for fibers

The useful way to express the attraction of dyes to fibers is by expressing it in terms of standard affinities. Since dyeing in most fibers is a thermodynamically reversible process, i.e. desorption is the reverse of sorption, so it is permissible to use thermodynamic functions for these dye fibre system [7, 10]. Only a brief explanation of the thermodynamic part will be discussed due to the fact that this study was performed at room temperature.

2.4.2 Sorption at dyebath fibre interfaces

In sorption of dyes by fibers there are forces involved and they may be non-specific (Van der Waals) forces, similar to the forces involved in liquefraction or formation of solution or stronger specific forces, such as those which are operational in the formation of chemical bond. It is told that when sorption takes place, dye molecules become immobilized if the sorption is localized, or they are restricted to two dimensional motions. The sorption processes are there for accompanied by a decrease in entropy, since sorption involves a decrease in free energy then form the thermodynamic relationship:

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

With the theory that all sorption processes are exothermic it is evident that ΔH must always be negative. The extent of sorption (under equilibrium conditions) therefore increases with decreasing temperatures [7, 10].

2.4.3 Sorption Isotherms

Usually the results of equilibrium dyeing measurements are expressed in the form of sorption isotherms in which the variation in the concentration of dye on the fiber with the concentration of dye in solution is followed. The effect of other variables is studied by observing the displacement of these concentration isotherms [15, 10, and 7]. The Langmuir, Freundlich and Nernst isotherms are the commonly used isotherms to classify dyeing isotherms even though they are more correctly applied to the adsorption of gases on metal surface. The Nernst and Freudlich will be described in short and Langmuir more broadly.

2.4.4 Nernst Isotherm

It is similar to Hanry's law for gases $[C]f = K[C]g$ ……(2)

Where $[C]_f$ and $[C]_g$ represent the concentration of dye in fiber and in the solution, K is the partition coefficient of dye between the fiber and bath.

2.4.5 The second Isotherm experimentally obtained by Freudlich in 1907

$[C]_f = K[C]_g^x$ …… (3)

Where K is the constant and x is characteristic exponent of the system being considered it normally oscillate between 0.5 to 0.8 according to the fiber and dye used. This isotherm is not valid for high concentrations, because generally the adsorption is limited by the saturation which the fibre is subjected to by the dye. The logarithmic of the equation

$log[C]f = log\,K + x\,log[C]g$ ……. (4) Equation of a straight line.

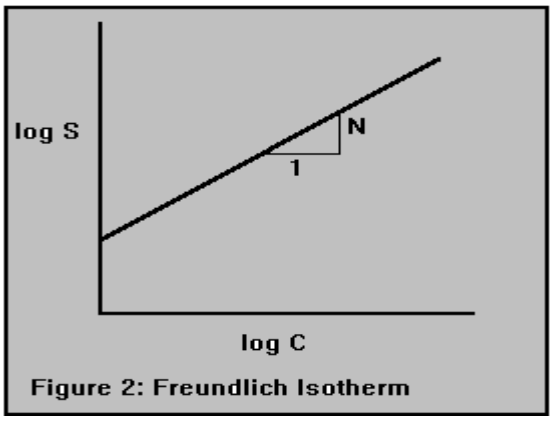


Figure 2: Freundlich Isotherm [15]

2.4.6 The sorption isotherm by Langmuir

This isotherm was obtained by starting from the kinetic principles of the dyeing process and combining it with his basic assumptions that the dye is absorbed by the fibre at specific sites. By this he meant when a molecule occupies a site, this becomes saturated and incapable of further adsorption.

For further illustration let suppose that a fiber contains $[C]_f$ moles of dye per kg of fiber, in equilibrium with a dye bath at a concentration of $[C]_s$ moles of dye per litre of solution in such a way that when all the sites of the fibre are occupied by the dye the concentration of these is $[C]_{sat}$. If the dye is continuously removed from the surface of the fiber it rate of desorption will be proportional to the concentration of the fiber.

$$d[C]f/dt = K1[C]f \quad (5)$$

At the same time the dye from the solution which arrives continuously at the surface of the fibre is adsorbed. The rate of adsorption with reference to the dye in solution which is equal to that in reference to the dye in the fibre but with a different sing (+)

$$-d[C]s/dt = d[C]f/dt \quad (6)$$

is proportional to the concentration of the dye in the solution and to the number of unoccupied sites which in its turn is proportional to $[C]sat - [C]f$ i.e.

$$-\frac{d[C]s}{dt} = \frac{d[C]f}{dt} = K2[C]s\,([C]sat - [C]f) \quad (7)$$

At equilibrium the rate of adsorption and desorption are equal so

$$K1[C]f = K2[C]s\,([C]sat - [C]f) \quad (8)$$

And supposing that $K2/K1 = K$ and solving for K in the above equation gives

$$K = [C]f\ /\ [C]s\,([C]sat - [C]f) \quad (9)$$

Where *K* becomes the equilibrium constant of the reaction

$$Colorant + non - dyes\ fiber \leftrightarrow dyed\ fibre$$

$$Cs \qquad Csat - Cf \qquad Cf$$

The final equation by calculating C_f become

$$[C]f = K[C]s[C]sat/\ 1 + K[C]s \qquad (10)$$

The isotherm drawn here between the axes has the form of a hyperbola

$[C]f\ vs\ [C]s\ \ where\ \boldsymbol{S}\ stands\ for [C]s\ and\ \boldsymbol{CL}\ represents\ [C]f$

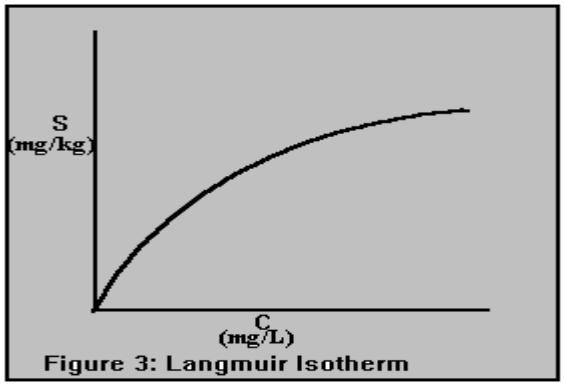


Figure 3: Langmuir Isotherm [15]

The form of equation (9) and (10) is not suited for studying the isotherm using graphs, however with simple transformations one can successively obtain three equations which can all be represented by strait lines. It is convenient to represent Langmuir ‘s in different way since with only one of these , experimental errors and the deviation of the law could pass unnoticed while using the other possibilities of representation of these can be made obvious.

$$\frac{1}{[C]f} = \frac{1}{[C]sat} + \frac{1}{K}[C]sat * [C]s \qquad (11)$$

$$\frac{[C]f}{[C]s} = K\ [C]sat - K\ [C]f \qquad (12)$$

$$\frac{[C]s}{[C]f} = \frac{1}{K}[C]sat + \frac{[C]s}{[C]sat} \quad (13)$$

Equation (11), (12) and (13) are the usually used for practical use and this will be illustrated in the experimental part.

Langmuir's isotherm differs from Freudlich's because in the former the value of the concentration of the dye in the fibre tends towards a limit of saturation while this is not the case in the latter. In practice satisfactory result are obtained with both equations although it is advisable to use Langmuir's equation when precise result are desired and Freudlich's when greater speed is wanted and greater accuracy is not necessary [7,8,10,15].

2.5 Influences of sorption process

Applied properties of textile fibers are determined by their sorption, mechanical and chemical characteristics, which depend on the chemical and sub-microscopic structure of the fiber. Since sorption process properties in fibers are best described by dyeability. To view these properties the structural differences of fiber have a large influence on dyeing kinetics, dyeability and the colour of fibers. Some are said to have greater influence on dye diffusion into the fiber, while others have a greater influence on dye uptake at equilibrium.

Under the field of structure/ dyeability interdependence analyses of two basic models of orientated polymer structure generally still predominate – the so called pore- model and free-volume-model. The pore-model is based on a presumption that, if the threshold of pore size is set low enough, all materials are porous. Dyestuff diffusion in pore-model occurs through a net of capillaries filled with water. The distribution of dyestuff occurs in accordance to a macroscopic sorption equilibrium, which means those pores are partly filled with dyestuff molecules. If the material absorbs the dyestuff according to the pore mechanism, satisfactory result are obtained under the following presumptions : the pore are not spherical, but in the form channel; these channels form a coherent network with the diameter, which is at least twice as large as the diameter of dyestuff molecules; the pores have to be accessible from outside. Where the free-volume-model or theory of free volumes is based on the concept of thermal movement of the macromolecules inside the fiber [9].

2.6 The kinetics of dyeing

The dyeing or sorption of dye to fiber is a complex subject as there are sub- theoretical processes involved to achieve the equilibrium. The first being the instantaneous chemical potential, also known as instantaneous affinity, is the measure of driving force of a dyeing process which is annulled when the dyeing process reaches equilibrium. Provided that the system is homogenous the absolute chemical potential is equal in every point and thus the concentration of dye will also be equal at equilibrium. The heterogeneous system has a behaviour different because even if the chemical potentials of the phases are equal, their concentration may be different, with this being said the dyeing equilibrium the solution will always have a lesser concentration of dye than the fibre. With this being the case it is affirm that if in any dyeing system there is difference in instantaneous chemical potential, a movement of material will take place from the higher towards the lower potential until they become level. Where else in the homogenous system the difference in concentration will be sufficient to cause the transport of matter. To further describe the process of transport caused by molecular movement, it can be stated that the transport mechanism of dye in dyeing process functions by means of diffusion.

The phases that take place during the dyeing process or sorption process of dye

a) Diffusion of the dye in the bath towards the surface of the fibre
b) Adsorption of the dye at the fibre surface
c) Diffusion of the dye within the fiber
d) Fixation of the dye within the fiber.

The dyeing rate is influenced by the first three partial phases cited above; even though they occur simultaneously it is necessary to find out which one of them is the slowest, since the rate of dyeing is determined precisely by that which has the smallest value. The comparison performed state that (a) will have very little influence, where the speed of adsorption is fast in comparison with the rate of diffusion within the fiber. The diffusion has principally more influence on the dyeing rate however absorption is considered since it the one measured [7, 10].

2.6.1 Diffusion importance within the fibre

The fiber dyeing depends a lot on diffusivity, this leads to the highlighting of what affect diffusion of dye. Among these factors the dimension of pores in the amorphous part of the fiber, state of aggregation of the dye, the crystalline structure of and the forces electrical repulsion [7, 10]. The size of dye governs the agglomeration and there are two theories that explain the state of aggregation which dyes must have in order that they diffuse easily through fibre.

One states that the dye in aqueous solution are in state of mono-molecular aggregation since in such a form they can easily diffuse and the other which put forward by Boulton and Morton, who affirm that the dye can be in solution both in a state of mono-molecular aggregation and in a macromolecular state, and that a dynamic equilibrium exists between them. What this really means is that the fiber only accepts the monomolecular particles and once these have been adsorbed, the equilibrium will move in the direction of splitting the large aggregations and supplying other new mononuclear particles which will tend to stabilize the equilibrium of the system [7, 10].

2.6.2 Fick's law of diffusion

In year 1855 Fick was the first to adopt the latter concepts developed earlier by Fourier. The hypothesis that he used state that the rate of transfer of a diffusant through a section of unit is proportional to the concentration gradient measured normal to section.

$$F = -D \frac{dC}{dx} \qquad (14)$$

F – Being the rate of transfer per unit area of section

C – Is the concentration of the diffusing substrate

X – Is the space co-ordinate measured normal to the section

D – Is the diffusion coefficient normally in m^2s^{-1}

$\frac{dC}{dx}$ is therefore the concentration gradient

This is known as Fick's first law which describes the rate of transfer in a steady state flow across the section. To predict the behaviour for non-steady state the Fick's second law is used which describes the accumulation of matter in a medium at a given point as a function of time [7, 10]

$$\frac{dC}{dt} = D\frac{d^2C}{x^2} \tag{15}$$

2.7 The empiric kinetic of dyeing

The determination of rate of dyeing is represented by using empiric kinetic equations which enables the specific speed constant to be calculated. The constants are characteristic of each dyeing system in which must be considered as well as the dye and the fibre, the bath ratio, and agitation. All kinetic studies are required to be performed at constant temperature.

2.7.1 First order equation

$$\frac{dCt}{dt} = K\,(C\infty - Ct) \tag{16}$$

After integration

$$Ct = C\infty\,(1 - e^{-kt}) \tag{17}$$

The first order equation presuppose that the rate of dyeing is directly proportional to the quantity of fibre not dyed which is represented by $(C\infty - Ct)$ where C is the quantity of dye at equilibrium, the equation gives a straight line.

2.7.2 Vickerstaff on his kinetic study of dyeing presented a hyperbolic type equation.

$$\frac{1}{C\infty - Ct} - \frac{1}{C\infty} = kt \tag{18}$$

The differential equation

$$\frac{dCt}{dt} = k\,(C\infty - Ct)^2 \tag{19}$$

Which is therefore a second order kinetic equation, it is not suitable for experimental result but it has the advantage that it can be applied to different values of exhaustion at equilibrium.

2.7.3 Cegarra-Puente is another useful equation to evaluate kinetics of dyeing.

$$\frac{Ct}{C\infty} = (1 - e^{-kt})^{\frac{1}{2}} \qquad (20)$$

Although the Cegarra-Puente equation was obtained from constant concentration baths, it can also be applied in dyeing to exhaustion if some opportune modifications are introduced to take account of the exhaustion of bath [7, 10].

2.7.4 Half time of dyeing and Hill's equation to determine diffusion coefficient

The following equation can be used to calculate the diffusion coefficient when the half-dyeing time $t_{1/2}$ is known.

$$D = 0.04919 \cdot \frac{l^2}{t_{\frac{1}{2}}} \qquad (21)$$

And when a cylinders with an infinite range and radius in bath with constant concentration, **Hill's** equation are frequently used.

$$D = 0.0632 \cdot \frac{r^2}{t_{\frac{1}{2}}} \qquad (22)$$

The useful equation of calculating the diffusion coefficient which does not depend on half time of dyeing is [20]

$$D = \frac{\pi * R^2 * a^2}{Ce^2 * 16} \qquad (23)$$

2.8 Filtration

Filtration is necessary in many engineering fields, material used for filtration media provide advantages of high filtration efficiency and low air resistance. Filtration fineness is one of the most important concerns for the filter media performance. Since the channels and structural elements of a filter must be matched to the scale (as small as 0.3 micrometer) of the particles or droplets that are to be captured in the filter, one direct way of developing high efficient and effective filter media is by using nanometer-sized fibers in filter structure. In general, because of the very high surface cohesion, tiny particles of the order of <0.5micrometer can be easily trapped in the electrospun nanofibrous structured filters and hence the filtration efficiency can be improved [11].

2.8.1 Characteristic of filtration

The main mechanisms in mechanical filtering actions are interception, inertial impaction and diffusion. Interception is the filtering mechanism where a moving particle is blocked when it encounter's a passageway or hole smaller than it self-particle of relatively lager than pore size will have greater chance of being caught by the interception.

2.8.2 Nanofiber application as a pre-filter in waste waster

The requirements of a pre-filter it should have an extremely large surface area, relating to high dirt-loading capacity. To achieve this, the fiber diameter used for pre-filter should be smaller so that the filter will have greater surface area for particle's adsorption and there will be better retention of small particles. Electrospun polyamide 6 nanofibrious webs with fiber diameter in the range of 30-110 nm were prepared and employed as a membrane material for water filtration due to their excellent chemical and thermal resistance as well as high wettability. The separation of targeted particles size ranging 10 -1μm was approximated to be 90% [18].

Historically asbestos fibers were used as pre-filter media and they were the best at that time, however it was discovered that asbestos fibers caused a health hazard, and then fine diameter glass and polymeric fibers were used to substitute it. The replacement material gave inferior performance compared to asbestos since the producing techniques available at

this time could not produce sub-micron fibers with large surface area [18]. In general, filtration efficiency will be higher when the fibers diameter is small and the pore diameter is small [11, 18].

2.9 Spectrophotometer

The spectrophotometry is a method based on measuring of the matter absorption of the electromagnetic radiation: in gases, liquids, mixtures thereof, solid materials and especially in diluted compound solutions. It is one of the basic laboratory analytical methods. It is utilized for both, simple measuring of the solution concentration and for analytical measuring for example:

- Defining of the chemical compounds contained in a solution
- Identification of conjugated structural parts of molecules
- Determining the type of the chemical bond of individual part of molecules
- Determining the type of the chemical bond of individual parts of molecules
- Determining of dissociation constants
- Defining the equilibrium state of kinetic reactions

$$E = h.f$$
$$= h\left(\frac{c}{\lambda}\right) \qquad (24)$$

E = photon energy

h = Planck constant

f = radiation frequency

λ = radiation wave length

c = light velocity in vacuum

Atoms, molecules, respectively their parts have completely characteristic electromagnetic radiation absorption of certain wavelengths. The photon absorption in an atom or molecule is possible only if their energy is equal to possible (acceptable) changes of the energy levels

of an absorbing atom or a molecule. Photon absorption from an ultraviolet or visible area cause mostly changes of energy levels of valence electrons. At the photon absorption from an infrared area, vibratory or rotational movements of many kids, characterized by their characteristic frequencies, are induced in molecules or their parts.

If the measured solution is coloured, it does not absorb all light wavelengths with the same intensity. It is so called selective absorption. Either individual spectral lines, or wider stripes, or even extensive spectral regions can be absorbed. Absorption spectrum develops by the passage of the white light through the absorbing environment. It is a negative supplement to the emission spectrum.

The spectrophotometer differs from simple photometers in that they are equipped with the monochromator.

Monochromator is the main spectrophotometer part. One colour- monochromatic-radiation beams created by the monochromator serves to determine the absorption related to the exactly defined radiation wavelength.

Some basic part of spectrophotometer:

- Radiation source
- Auxiliary optical system
- Dispersion system: optical prism or optical grating
- Slot diaphragm
- Cell with examined substance
- Radiation detector: photocell, photoelectric cell, photomultiplier
- Indicator or recording instrument

Spectrophotometer quality

Depends on the quality of chromometer, on narrower zone of the wave lengths in the metering beam is the chromometer able to provide, or the smaller is the width of the spectrum interval, the better is the instrument. With the quality instrument it is in order of 0.1 nm. The width of spectrum interval term is sometimes confused with the width of the slot diaphragm term. Fulfilment of the Lambert-Beer law is dependent on meeting the

condition of the smallest spectral interval width. With the greater spectral interval width, deviations from the L-B law linearity can be found and this can have an unfavourable effect on, for example, determining the sample concentration by calculation, based on knowledge of the molar absorption coefficient [19].

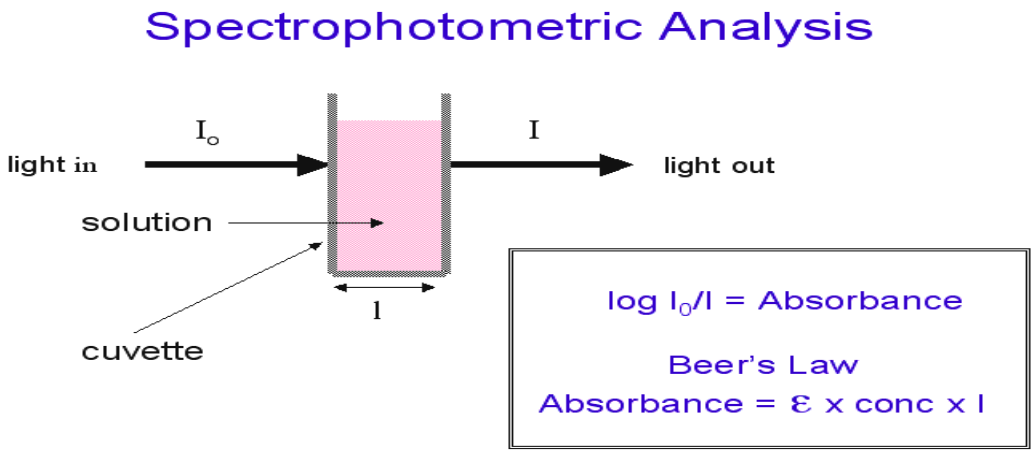


Diagram 3: shows the description of spectrophotometer used in practice [16]

It is simple, so called one-ray spectrophotometer for metering in the visible zone (the exact wave lengths range is 340 to 850 nm), with manual control (Spekol 11, Carl Zeiss, Jena) and digital output value of the measured factor (absorbance, permeability, concentration, fluorescence). Monochromator is equipped with the optical grating with 651 "scratches" for 1 mm. The spectral interval width is 11 nm. The vacuum photocell is used as a radiation detector. There are actually two photocells in the instrument, a "red" one –for metering in long wave zone and a "blue" one for the short wave spectral zone [16, 19].

3 Experimental part

3.1Objective of experiments

1) Comparison of the rate (kinetics) of dyestuff in standard fibers and in nanofibers, experimental result must be analyzed by theoretical models
2) To compare the equilibrium of dyestuff sorption in standard fibers and in nanofibres, experimental result should be analyzed by theoretical I isotherms.
3) Simulation of dye removal from wastewater using sorption-filtration method, different acid dyestuff used for comparison of sorption.

Used instrument for measuring

Diagram 4

The spectrophotometer was used for analytical part of the experiments where all the sorption experiments performed in this study were analyzed by it. The wavelength of each type of dye used was set with respect to the dyestuff used.

3.2 Analytical procedure

The concentration chosen for this study was low, which lead to the use of a bigger cuvette so as to analyze the solutions accurately. The spectrophotometry machine was always switched on 30 minutes before the measurements were performed to warm up the spectrophotometer. Deionized water was used for calibration. The wavelength setting for each dye was performed by measuring the blank solution (which was from stoke solution of used concentration 0.01 g/L) different wavelength were tested until the highest absorbency was obtained and that value was chosen as the wavelength setting for that particular dyestuff.

When the wavelength was set the absorbency after absorption or sorption experiment was measured which was represented as ***At*** for all experiments and the original blank concentration described by ***Ao***. The cuvette was dried every time before it was inserted to the spectrophotometer to make sure there was nothing on it walls that could interfere with the light which detects the absorbency and it was made sure that the measured sample had no solid particles that could alter with the absorbency reading as the spectrophotometers are sensitive.

Table 1: represent the chosen wavelength for each dye used in experimental part

Dye used	Wavelength used for measuring absorbency (nm)
C.I. Acid blue 113	570
C.I. Acid yellow 40	402
C.I. Acid red 118	490
C.I. acid blue 41	590

3.3Kinetics experiments and procedure

3.3.1Material used

The kinetics experiments in sorption are performed to determine the rate of sorption of sorbate molecules on to the surface of sorbent to the interior structure of the sorbent material and to estimate when the equilibrium time will be reached. The dye used for kinetic and equilibrium study was C.I Acid blue 113 obtained from Technical University of Liberec. The Polyamide 6 nanofiber sample with specific area density of 12 g/m^2 was obtained from Elmaco Company from Czech Republic was used as the sorbent material. The other sorbent material used was standard polyamide 6 which was also obtained from Technical University of Liberec.

3.3.2 Preparation and procedure

The dye stock solution was prepared by dissolving 500 mg of C.I Acid blue 113 in 0.5 L of deionized water where 0.02 L from the total volume of 0.5 L was heated up to warm temperature to premix the dye powder to make the dye solubility better and the balance of water added after. The stock solution concentration obtained was 1000 mg/L where from this concentration dilutions were performed to simulate the waste water concentration which was 10 mg/L and this was the concentration which was used for all experiments of kinetics, equilibrium and sorption filtration process.

The sample size used for nanofibers was estimated by measuring the area of 30*30 mm and the mass of the sample was calculated based on this area. The same was applied for standard fiber but the mass was weighed in the mass balance. The conical flask were used for reaction and there were closed during the experiments to prevent evaporation of solution, the solutions were also kept in the closed shelf to prevent light radiation which can interfere with kinetics experimental reaction. The kinetics experiments were performed at room temperature and constant volume of 100 ml of liquor in each conical flask.

Table 2 (Kinetic experimental results of nanofibers)

Time [min]	CL [g/l]	% Exhaustion	Cs [mg/g]
1	0.0099	0.54	0.50
5	0.0099	0.98	0.90
10	0.0098	2.39	2.21
20	0.0098	2.50	2.31
30	0.0095	5.21	4.83
45	0.0094	5.75	5.33
60	0.0093	6.95	6.43
90	0.0091	9.12	8.44
120	0.0090	10.31	9.55
150	0.0088	11.51	10.66
180	0.0089	10.94	10.13
300	0.0085	14.81	13.71
360	0.0082	17.70	16.39
420	0.0084	15.99	14.80
1440	0.0048	51.71	47.88
1440	0.0048	52.24	48.37
4320	0.0032	67.97	62.93
5760	0.0045	54.99	50.92
10080	0.0028	71.86	66.54
11520	0.0030	69.60	64.45
11880	0.0022	78.41	72.60
14400	0.0019	80.67	74.69

3.3.3 Sample calculations and results

This represents the basic calculations performed for each calculated parameter in the tables based on measured values and the calculations performed were similar for nanofibers and also standard fibers. This was how the kinetic tables and equilibrium tables were obtained based on the following calculations.

CL: concentration in liquor after the end of each sorption experiment with respect to the day it was stopped calculated from $\boldsymbol{CL = CLo\ (At/Ao)}$

CLo: being the original concentration = **0.01 (g/L)** which was used for all experiments.

Ao: the original absorbency obtained from spectrophotometer which in this case was **0.921**

At: represents the absorbency after the end of each sorption experiment with respect to the day it was stopped.

Exhaustion on fiber calculation

$$\%\boldsymbol{E} = \left(\frac{\boldsymbol{Ao - At}}{\boldsymbol{Ao}}\right) * \mathbf{100}$$

$\boldsymbol{Cs}$: Ratio of mass of dye in fiber per mass of fiber was calculated with the following equation

$$\boldsymbol{Cs} = \frac{\boldsymbol{mD}}{\boldsymbol{mF}} \; where \; \boldsymbol{mD} \; mass \; of \; dye \; in \; fiber \; and \; \boldsymbol{mF} \; mass \; of fiber$$

$$\boldsymbol{mD} = \boldsymbol{CLo} * \boldsymbol{V} * \%\boldsymbol{E} \qquad where \, V \, represant \, the \, volume \, of \, liquor \; 0.1L$$

$$\boldsymbol{mF} = \boldsymbol{A} * \boldsymbol{Surface} : surface \; density \; used \; 12 \left(\frac{g}{m^2}\right) and \; A \; is \; the \; area \; of \; sample$$

$$\boldsymbol{A} = 0.03 * 0.03 = 0.0009 \; m^2$$

The area was constant for both standard and nanofibers

$$mF = 0.0009 * 12 = 0.0108 \; g \;\; this \; value \; was \; constant \; for \; all \; kinetic \; experiments$$

The mass of standard fibers was estimated by weighing balance while the nanofiber mass was calculated as the above calculation.

$$\boldsymbol{mD} = 0.01 * 0.1 * 0.0005 = 5.4 * 10^{-6} \;\; note \; that \; \%E \; is \; the \; only \; changing \; variable$$

$$Cs = \left(5.4 * \frac{10^{-6}}{0.0108}\right) * 1000 = \; 0.54 \frac{mg}{g}$$

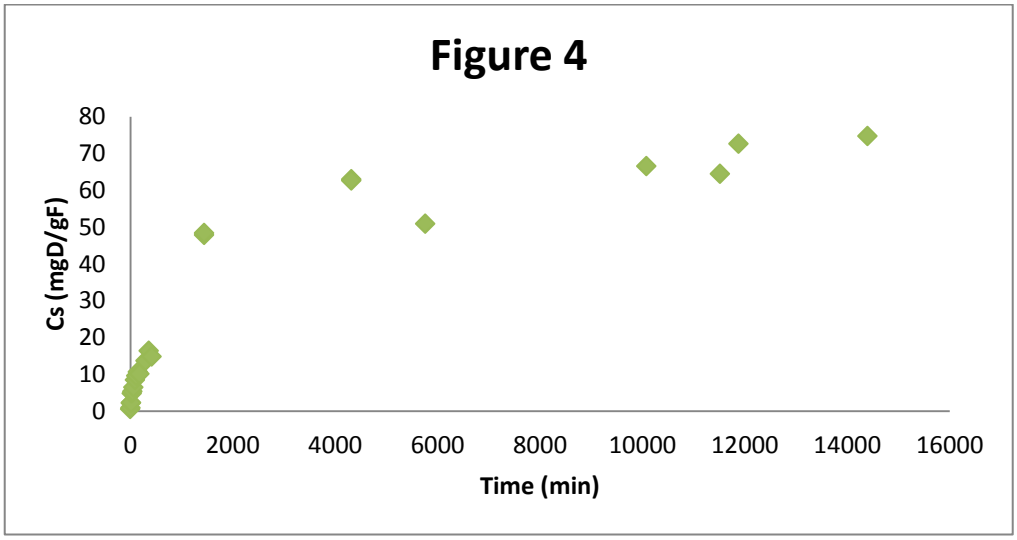


Figure 4: above represents the kinetics experimental results nanofibers which were obtained in total time of 10 days as the kinetic sorption was relatively slow to reach equilibrium.

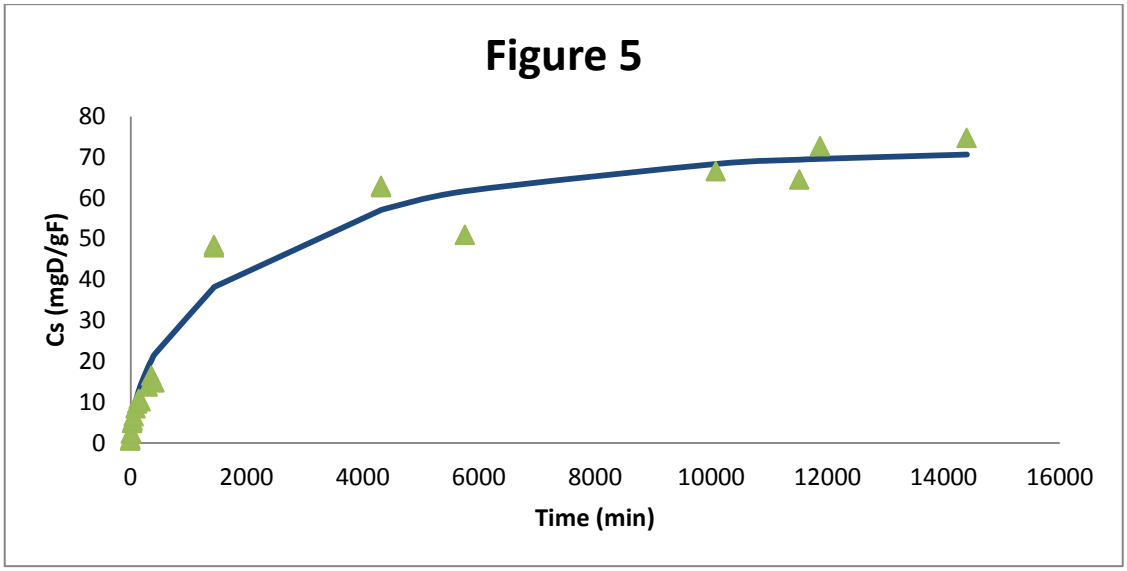
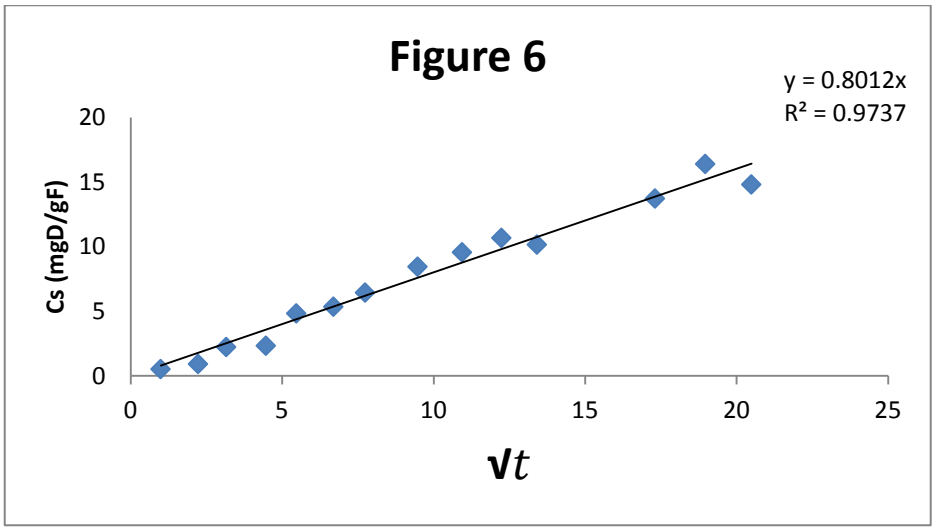


Figure 5: represents the kinetics experimental results which are dots and where the solid blue line represents the theoretical model $\frac{Ct}{C\infty} = (1 - e^{-kt})^{\frac{1}{2}}$ by Cegarra-Puente equation .

Discussion of kinetic results

The rate of sorption or dyeing was relatively slow as it took long time to reach equilibrium. Different types of theoretical models were used to model the experimental data from first order kinetic equation, second order kinetics and Cegarra-Puente equation. However the Cagarra-Puente's equation was the best fit model to describe the behavior of the nanofibers kinetics with C.I Acid blue 113 dye stuff result and for standard fibers as well.

Diffusion coefficient estimation



The diffusion coefficient estimation, the following equation was used $D = \frac{\pi * R^2 * a^2}{Ce^2 * 16}$ where *R* is the radius of fiber and *Ce* is the equilibrium value from experimental data and *a* is obtained from the plot of $\boldsymbol{Cs\ vs\sqrt{t}}$ in **figure 6** which gives the linear correlation. The second equation used was Hill's equation to estimate the diffusion coefficient for half time dyeing $D = 0.0632\,.\frac{r^2}{t_{\frac{1}{2}}}$ this equation requires the half time of dyeing which was estimated from kinetics experimental data

Standard fiber kinetic experimental result to be $t_{\frac{1}{2}} = 1300\ min$ and $\mathbf{r^2}$ is the radius of fiber.

$D = \frac{\pi * R^2 * a^2}{Ce^2 * 16}$	
R *a* *Ce* *Calculated D*	120 nm 0.8012 72 (mg/g) 0.35 (nm^2/ min)
$D = 0.0632 . \frac{r^2}{t_{\frac{1}{2}}}$ Hill's Equation	
r $t_{1/2}$ *calculated D*	120 nm 1300 min 0.70 (nm^2/min)

3.3.4 Kinetic experimental result of standard fibers

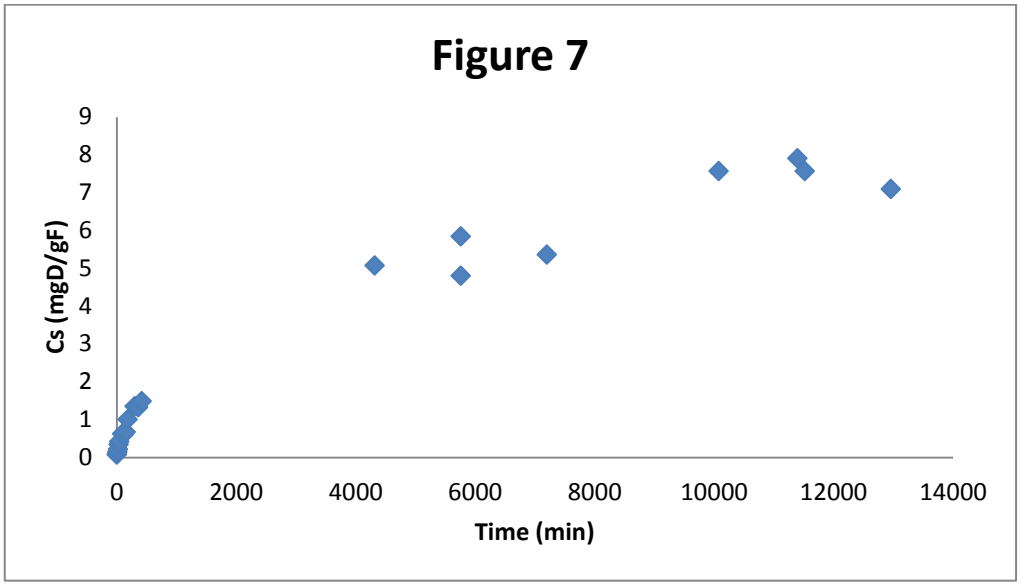


Figure 7: represents kinetic experimental result where concentration of dye in substrate was drawn vs time taken to reach equilibrium.

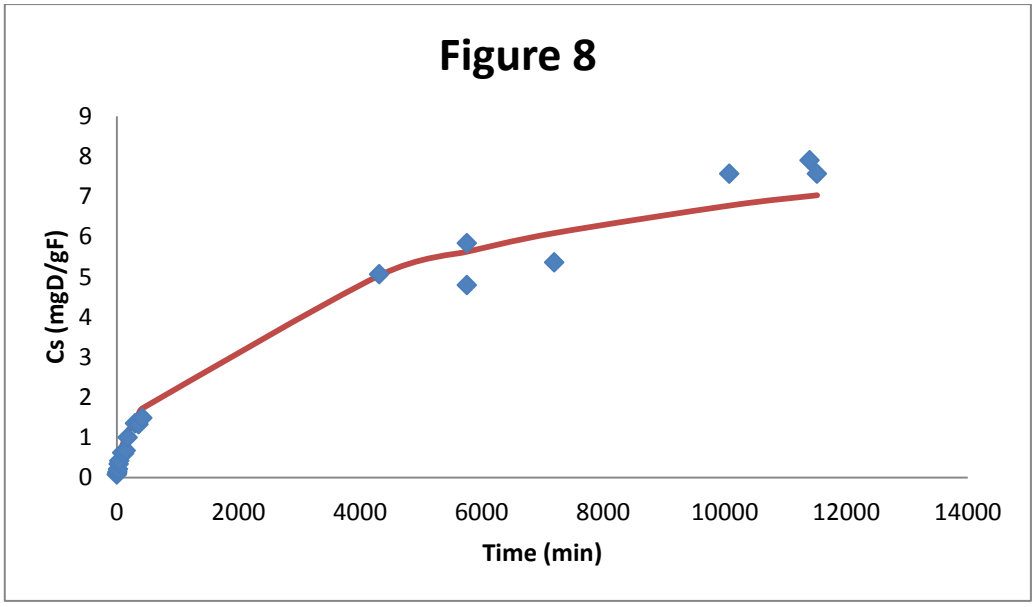


Figure 8: represents the experimental results which are dots and where the solid red line represents the theoretical model of Cegarra-Puente.

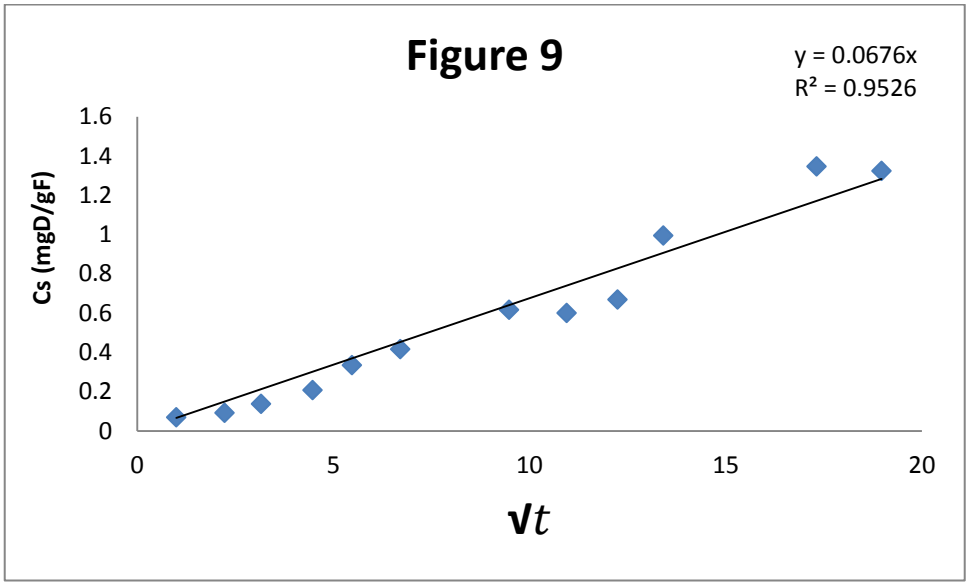


Figure 9: represent a linear correlation when Cs is plotted against square root of time to estimate the *a* constant to calculate the diffusion coefficient.

$D = \frac{\pi * R^2 * a^2}{Ce^2 * 16}$	
R	10000 nm
a	0.0676
Ce	8.5 (mg/g)
Calculated D	1241.3 (nm^2/ min)
$D = 0.0632 . \frac{r^2}{t_{\frac{1}{2}}}$ Hill's equation for half time dyeing	
r	10000 nm
$t_{1/2}$	2800 min
calculated D	2257.1(nm^2/min)

3.3.5 Discussion of result

The equilibrium time was 10 days which is represented in minutes in the tables of result for both standard and nanofibers. The equilibrium concentration is high in nanofibers when compared to standard fibers this can be caused by the large surface area that nanofibers offer. Calculating the ratio of standard fiber over nanofiber diffusion coefficient which was not related to half time of dyeing the value of 3547 was obtained, which can be related to the complexity of polymer substrates used.

3.4 Equilibrium experimental procedure and result

The equilibrium experiments of dyeing were performed based on the equilibrium time obtained from kinetic experiments which was 10 days to represent the dye distribution between the dye bath and the substrate. The same experimental procedure as kinetics experiments were followed for preparation liquor and sample sizes, the only different part lies with the fact that the mass of substrate and volume of liquor were not constant .The table below represents the variation of the changing variables; the temperature was constant which was at room temperature +/- 22 degrees. The theoretical models are usually used to describe the experimental result behavior.

Table 3 (equilibrium experimental result for standard fibers)

Volume (ml)	At	%E	mF [g]	CL [g/l]	CS [mg/g]
100	0.03	96.74	0.57	0.0003	1.697
100	0.036	96.09	0.38	0.0004	2.529
100	0.041	95.54	0.285	0.0004	3.352
100	0.041	95.54	0.475	0.0004	2.011
100	0.068	92.61	0.19	0.0007	4.874
100	0.276	70.00	0.095	0.0030	7.368
100	0.278	69.78	0.095	0.0030	7.345
100	0.35	61.96	0.095	0.0038	6.522
150	0.424	53.91	0.095	0.0046	8.513
200	0.555	39.67	0.095	0.0060	8.352

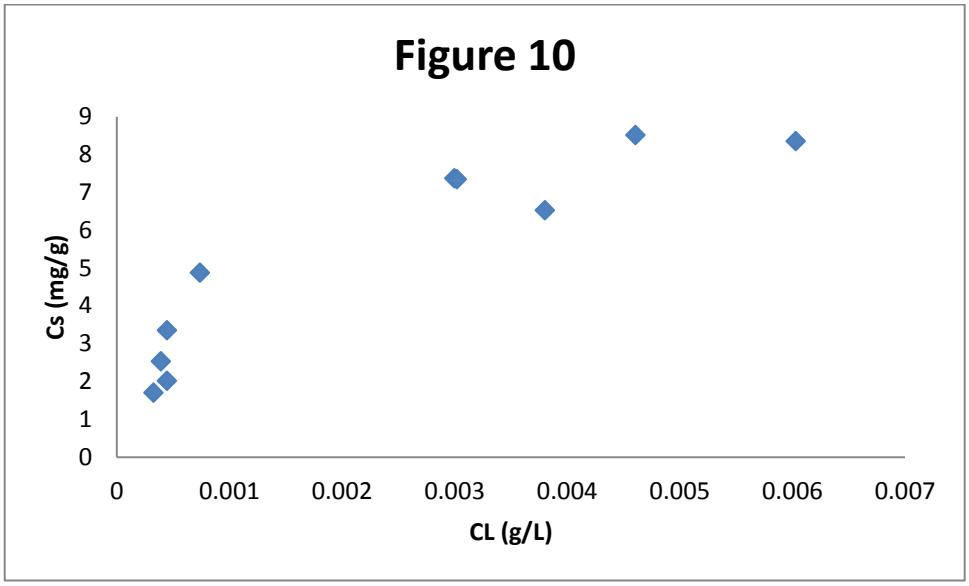


Figure 10: above represents the equilibrium experimental result obtained after 10 days using PA 6 standard fibers as sorbent material.

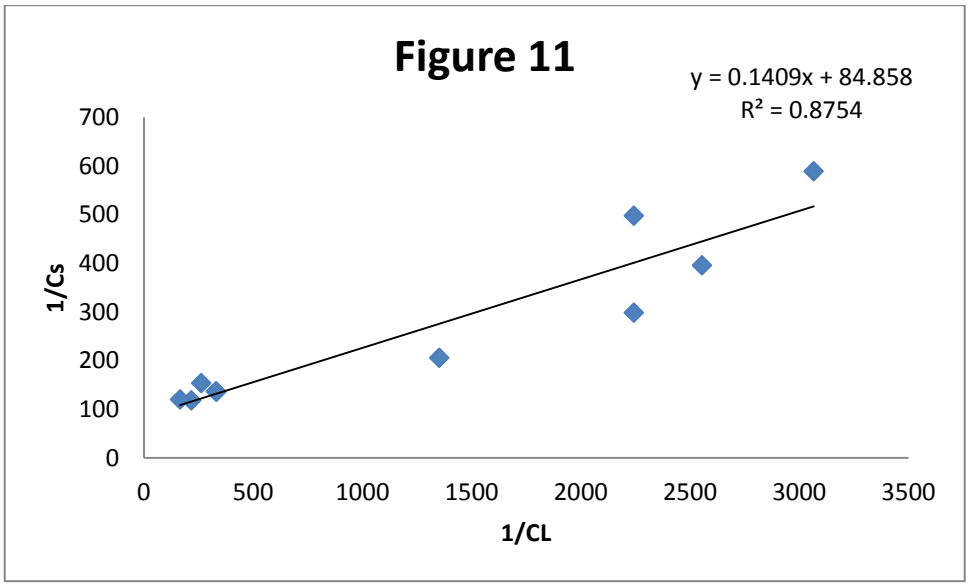


Figure 11: above represents a linear graph used to estimate Langmuir constants a and b from experimental result.

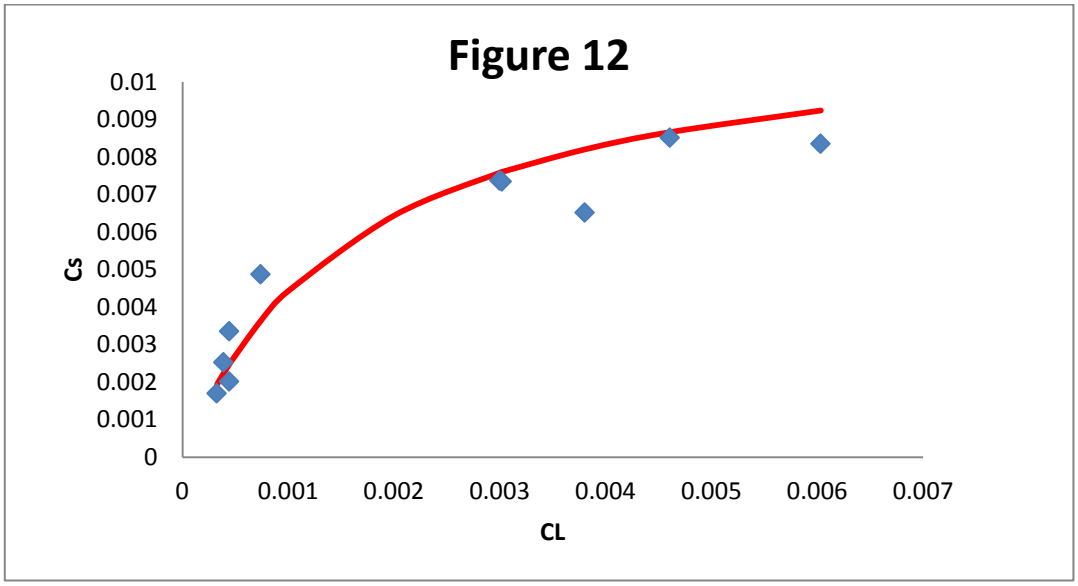


Figure 12: above represents experimental data in dots and the solid red line represents the theoretical model used which was Langmuir that described the dye distribution between fiber and liqour.

Table 4 (Nanofibers equilibrium experiments)

Volume (ml)	At	%E	mF [g]	CL [g/l]	CS [g/g]	CS [mg/g]
100	0.014	98.48	0.0756	0.00015	0.013	13.03
100	0.018	98.04	0.0432	0.00020	0.023	22.70
100	0.024	97.39	0.054	0.00026	0.018	18.04
100	0.032	96.52	0.0324	0.00035	0.030	29.79
100	0.041	95.54	0.0216	0.00045	0.044	44.23
100	0.177	80.76	0.0108	0.00192	0.075	74.78
100	0.185	79.89	0.0108	0.00201	0.074	73.97
100	0.211	77.07	0.0108	0.00229	0.071	71.36
150	0.347	62.28	0.0108	0.00377	0.087	86.50
200	0.486	47.17	0.0108	0.00528	0.087	87.36

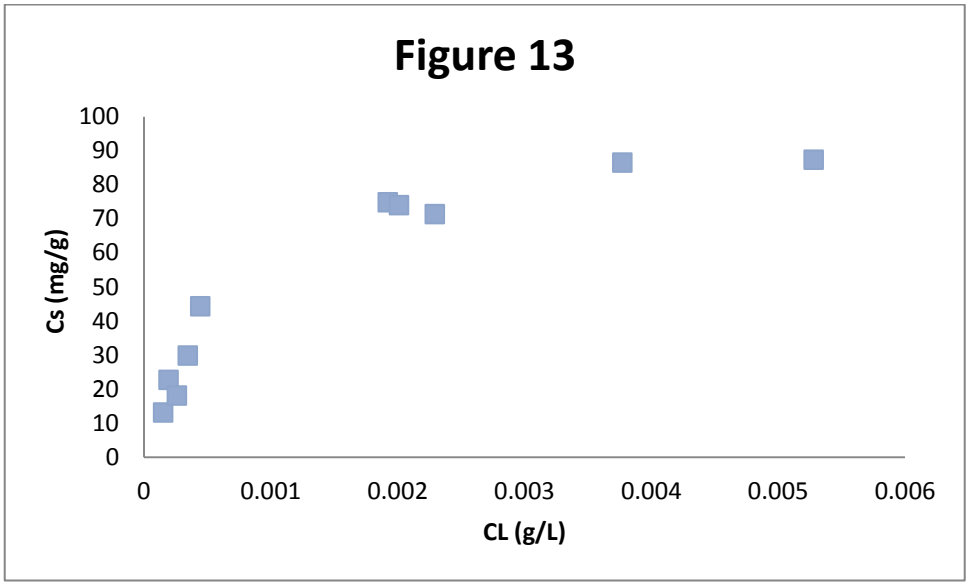


Figure 13: above represents the equilibrium experimental result of nanofibers as a sorbent material obtained after 10 days

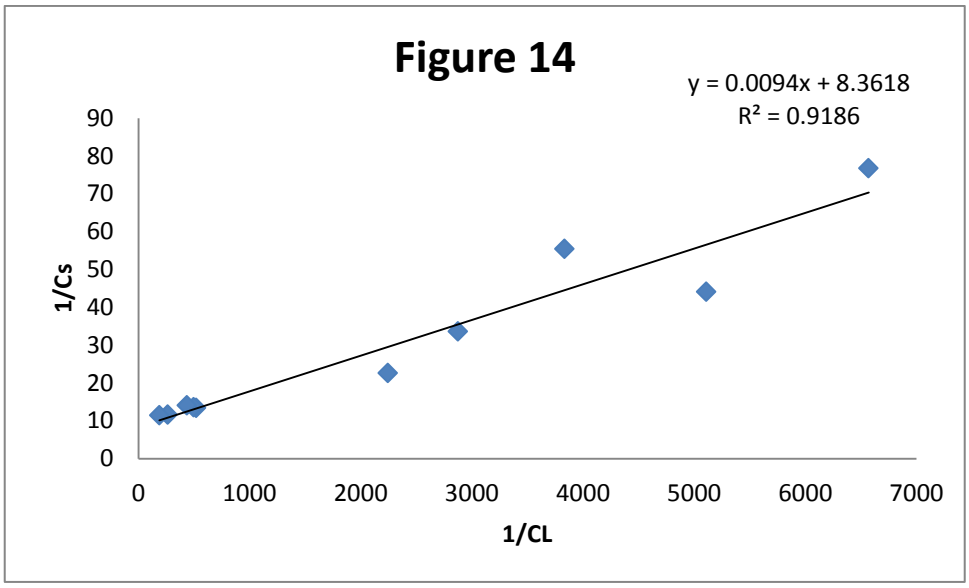


Figure 14: above represents a linear graph used to estimate Langmuir constants a and b form experimental results.

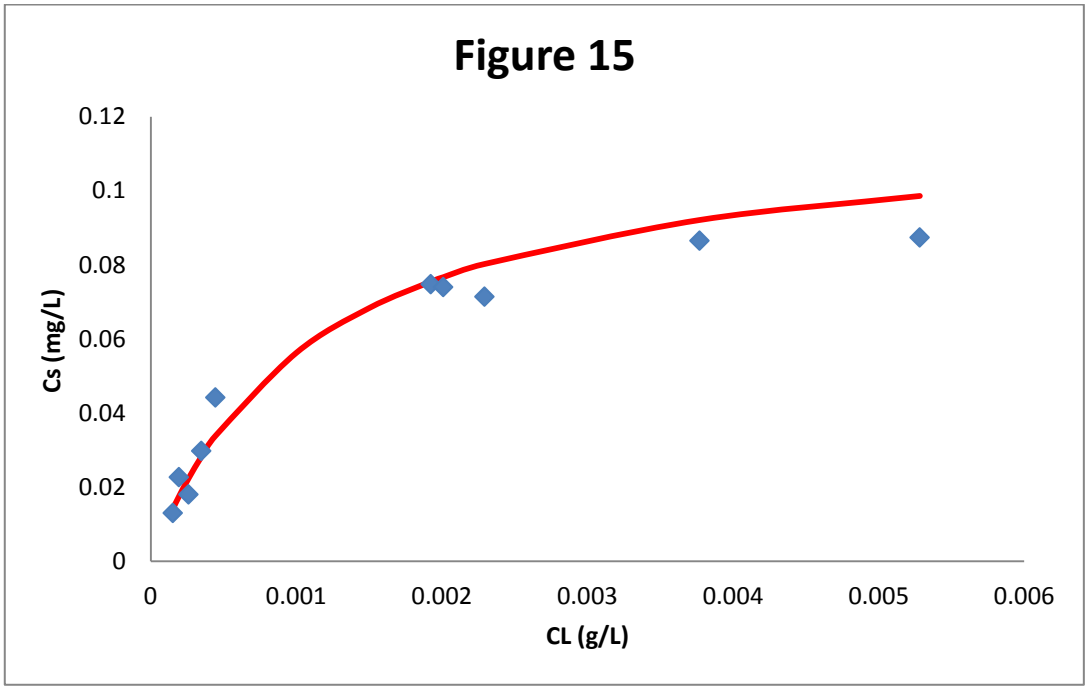


Figure 15: above represent experimental data in form of blue dots and the solid red line represents the theoretical model used which was Langmuir model to describe the dye distribution between fiber and liquor.

3.4.1 Sample calculations of Langmuir isotherm constants

The equilibrium isotherms are used to model the experimental result as to which isotherm will best describe the obtained experimental result. Amongst all isotherms Langmuir was the one which best described all the equilibrium experiments from standard to nanofibers. The standard equations used are as follows:

$$Cs = \frac{K\ CL.S}{1+KCL}\ Langmuir\ equation\quad K\ and\ S\ are\ constants\ which\ are\ calculted$$

Where:

$$K = \frac{1}{a} * S \qquad and\ \ S = \frac{1}{b} \qquad a\ and\ b\ are\ obtained\ from\ the\ plot\ of\ \frac{1}{Cs}\ vs \frac{1}{CL}$$

Standard fiber constants calculated	**Nanofiber constants calculated**
K = 602.2569 *S* = 0.011784	*K* = 889.5532 *S* = 0.119591

3.4.2 Discussion of equilibrium result

Theoretically the *K* equilibrium constant value should be the same for nanofibers and standard fibers because the same dyestuff, temperature, concentration and same substrate polyamide 6 was used but with different size in terms of nano and micro. With the Langmuir constant *K* values obtained there is not much of the biggest difference so it is not far away from theory.

The Langmuir saturation value *S* described the dye distribution for standard fibers as 10 times lower than the nanofibers this can be related to the large surface area properties that nanofibers offer and it could also be connected with the crystallinity where amorphous part of standard fiber could be too different from nanofibers because of its size.

3.5 Remission experiment

Colour comparison of nanofibers and standard fibers using samples from equilibrium and kinetics.

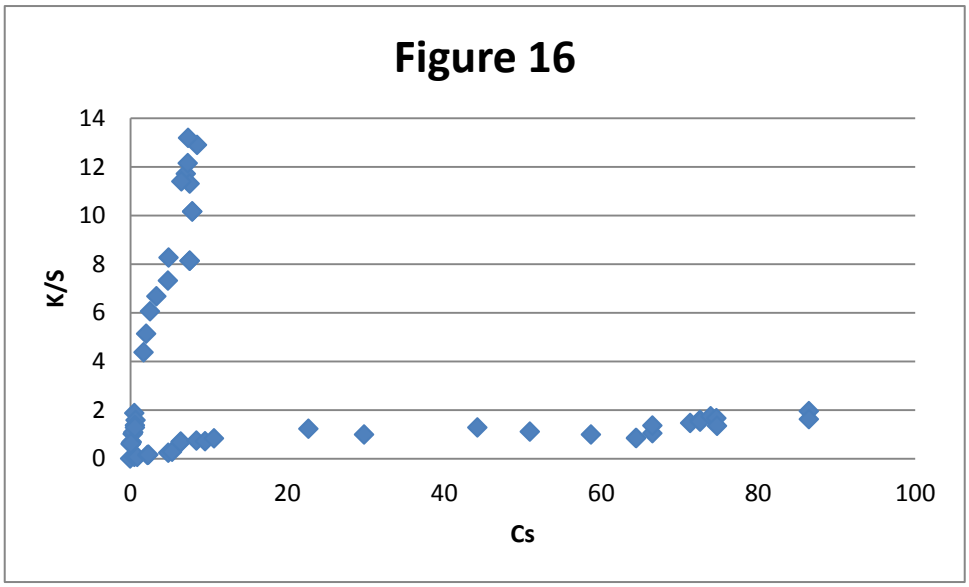


Figure 16: graph of standard fibers which have much stepper linear line and nanofibers with linear line close to the x axis. Kubelka Munk theory of remission that the above figure presents.

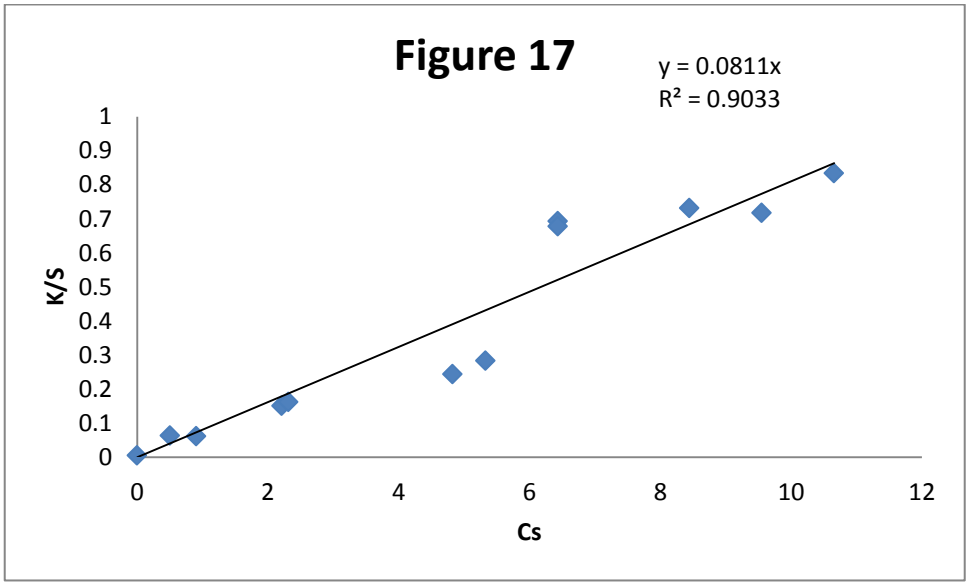


Figure 17 : Nanofiber linear relation to estimate constant *a* from the plot of K/S vs Cs based on remmision results on table .

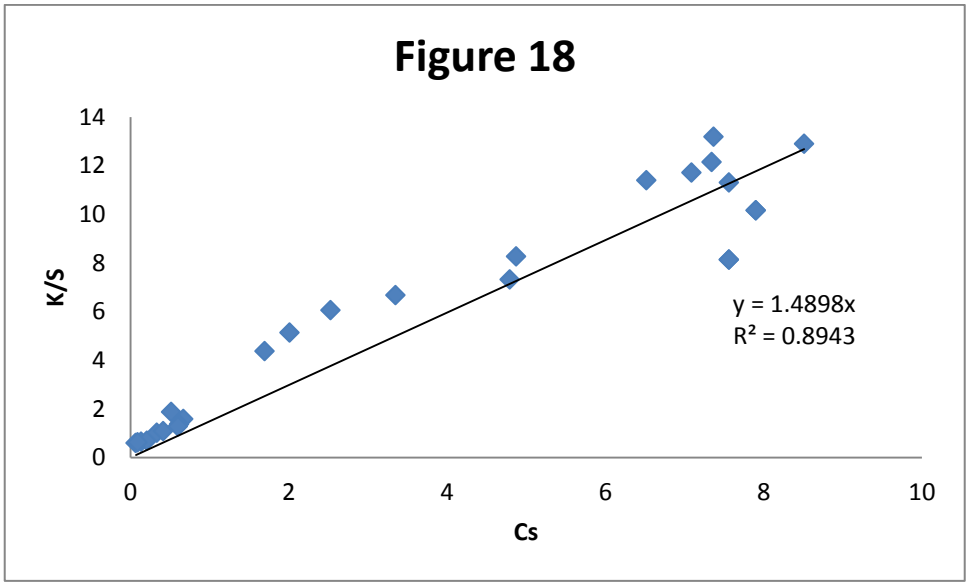


Figure 18: Standard fiber linear relation to estimate *a* from the plot of K/S vs Cs based on remmision results on table .

Table 5 (Remission and calculated K/S based on equilibrium and kinetics experiments)

Table 6 (Remission and calculated K/S based on equilibrium and kinetics experiments)

Standard fibers	
Cs	K/S
7.564023	8.137216
7.564023	8.137216
0.515928	1.864059
7.089151	11.70922
4.79394	7.314439
7.903217	10.16067
7.903217	10.16067
7.564202	11.30681
0.138504	0.641881
0.669437	1.577581
0.069252	0.597505
0.207756	0.683396
0.334718	1.015105
0.415512	1.077714
0.092336	0.620675
0.616343	1.36717
0.600185	1.281443
8.512586	12.89923
6.521739	11.39333
7.345538	12.14017
7.368421	13.18904
4.874142	8.266459
3.352403	6.673096
2.528604	6.056631
2.011442	5.135209
1.697178	4.368327

Nanofibers	
Cs	K/S
0	0.004661
0.502674	0.063338
0.904814	0.061521
2.211767	0.150328
2.312301	0.161366
4.825673	0.243029
5.328347	0.282856
6.43423	0.693057
6.43423	0.677562
8.444927	0.730923
9.55081	0.717054
10.65669	0.833789
22.69525	1.223631
29.79066	0.981416
44.23309	1.277564
50.92095	1.102389
58.72817	0.991138
64.44683	0.840741
64.44683	0.840741
66.53539	1.040808
66.53539	1.354157
71.35668	1.462405
72.60214	1.576562
72.60214	1.576562
72.60214	1.519121

3.5.1 Result discussion

The use of Kubelka Munk equation and the plot of K/S vs. Cs, taking the ratios of *a* for both nanofibers and standard fibres indicates that the colour is 20 less on the nanofiber substrate. With the theory of ratio of diameters of fibre should be the same as the ration of *a* here it not the case: ratio of diameters 83 and the ration of constant a 20.

3.6 The sorption-filtration method

With the increasing demand of finding alternative sorbents that can remove the colour from textile wastewater and also some other concerns about removing small size particles present in waste water treatment lead to more interest in nanofibers as a sorbent materials. Since nanofibers offer high surface area and they are cheap to produce they have more potential to be used in filtration and other parts of purification. In this part of experiment a new experimental method of testing the nanofibers as sorbent material to remove dye from waste water was introduced.

3.6.1 Experimental Method, apparatus and results

Four acid dyes **C.I. Blue 113, C.I. Blue 41, C.I. Yellow 40** and **C.I. Red 118** which were obtained from the university in a form of powder and deionized water were used to prepare the stock solution of 1000mg/L concentration, from the stock solution dilution of concentration was done to simulate the concentration of waste water which was 10 mg/L and in one experiment a 100 mg/L was used. Electrospun Polyamide 6 nanofibers were used as sorbent material which was obtained from company Elmarco s.r.o. The polyamide 6 nanofibers used were 5 g/m^2, 1 g/m^2 and 12 g/m^2 in areal density, the tables and graphs below illustrate the number of layers used and the difference was observed. The sorption – filtration process was performed under vacuum pressure created by suction pump where the vacuum flask was used to collect the filtered sample and the volume used per each cycle was 10 ml, test tubes were used to store the filtered solution samples. Acid dyes were used because of their high affinity to polyamide.

Apparatus used

1. Filtration funnel
2. Polyamide 6 nanofiber (Sorbent)
3. Filter supporting unit
4. Vacuum pressure port
5. Vacuum flask

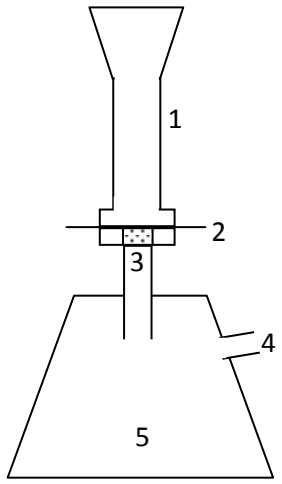


Diagram 5:*sorption-filtration process*

Analytical method: For testing the sorption capacity of the electrospun polyamide 6 nanofibers the spectrophotometer was used to measure the initial concentration of unfiltered sample and also the final concentration of filtered sample at selected wavelength which are presented on table 1. The stop watch was used to time each cycle. Parameters presented on the following graphs of result were calculated.

Table 7 (Sorption-filtration experimental results of C.I. Blue 113)

No of cycles	Time of flow [s]	concentration of dye in liquor after filtration [mg/L]	Change in mass of absorbed dye[mg]	accumulated mass of absorbed dye[mg]	Accumulative volume[L]	% of dye removed	% (mass of dye/ mass of fabric)
1	24	0.50	0.095	0.095	0.01	95.0	7.0
2	24	2.33	0.077	0.172	0.02	76.7	12.7
3	27	4.56	0.054	0.226	0.03	54.4	16.7
4	28	6.50	0.035	0.261	0.04	35.0	19.3
5	29	7.56	0.024	0.286	0.05	24.4	21.2
6	32	8.61	0.014	0.299	0.06	13.9	22.2
7	34	8.94	0.011	0.310	0.07	10.6	23.0
8	36	9.50	0.005	0.315	0.08	5.0	23.3
9	40	9.61	0.004	0.319	0.09	3.9	23.6
10	42	9.72	0.003	0.322	0.1	2.8	23.8
11	45	9.72	0.003	0.324	0.11	2.8	24.0

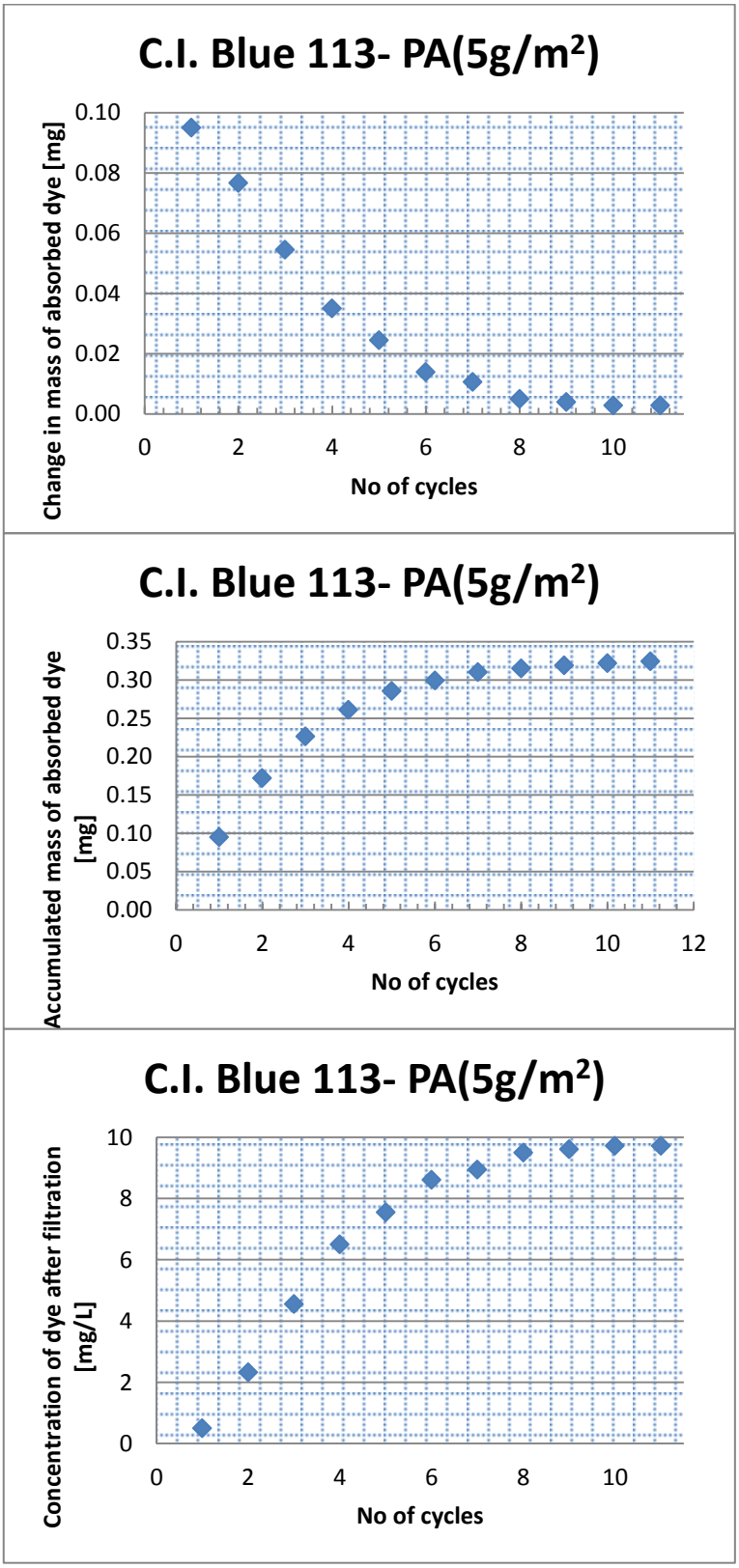


Figure 19 (represents the combination of three graphs drawn using data from table 7)

Table 8 (Sorption-filtration experimental results of C.I. Blue 113)

No of cycles	Time of flow [s]	concentration of dye in liquor after filtration [mg/L]	Change in mass of absorbed dye[mg]	accumulated mass of absorbed dye[mg]	Accumulative volume [L]	% of dye removed	% (mass of dye/ mass of fabric)
1	27	0.95	0.090	0.090	0.01	90.5	6.7
2	30	3.57	0.064	0.155	0.02	64.3	11.5
3	30	5.71	0.043	0.198	0.03	42.9	14.6
4	31	7.26	0.027	0.225	0.04	27.4	16.7
5	32	7.86	0.021	0.246	0.05	21.4	18.3
6	34	8.69	0.013	0.260	0.06	13.1	19.2
7	34	9.17	0.008	0.268	0.07	8.3	19.8
8	39	9.23	0.008	0.276	0.08	7.7	20.4
9	40	9.11	0.009	0.285	0.09	8.9	21.1
10	43	9.11	0.009	0.293	0.1	8.9	21.7
11	45	9.11	0.009	0.302	0.11	8.9	22.4
12	46	9.17	0.008	0.311	0.12	8.3	23.0
13	49	9.05	0.010	0.320	0.13	9.5	23.7
14	53	9.05	0.010	0.330	0.14	9.5	24.4
15	56	9.05	0.010	0.339	0.15	9.5	25.1

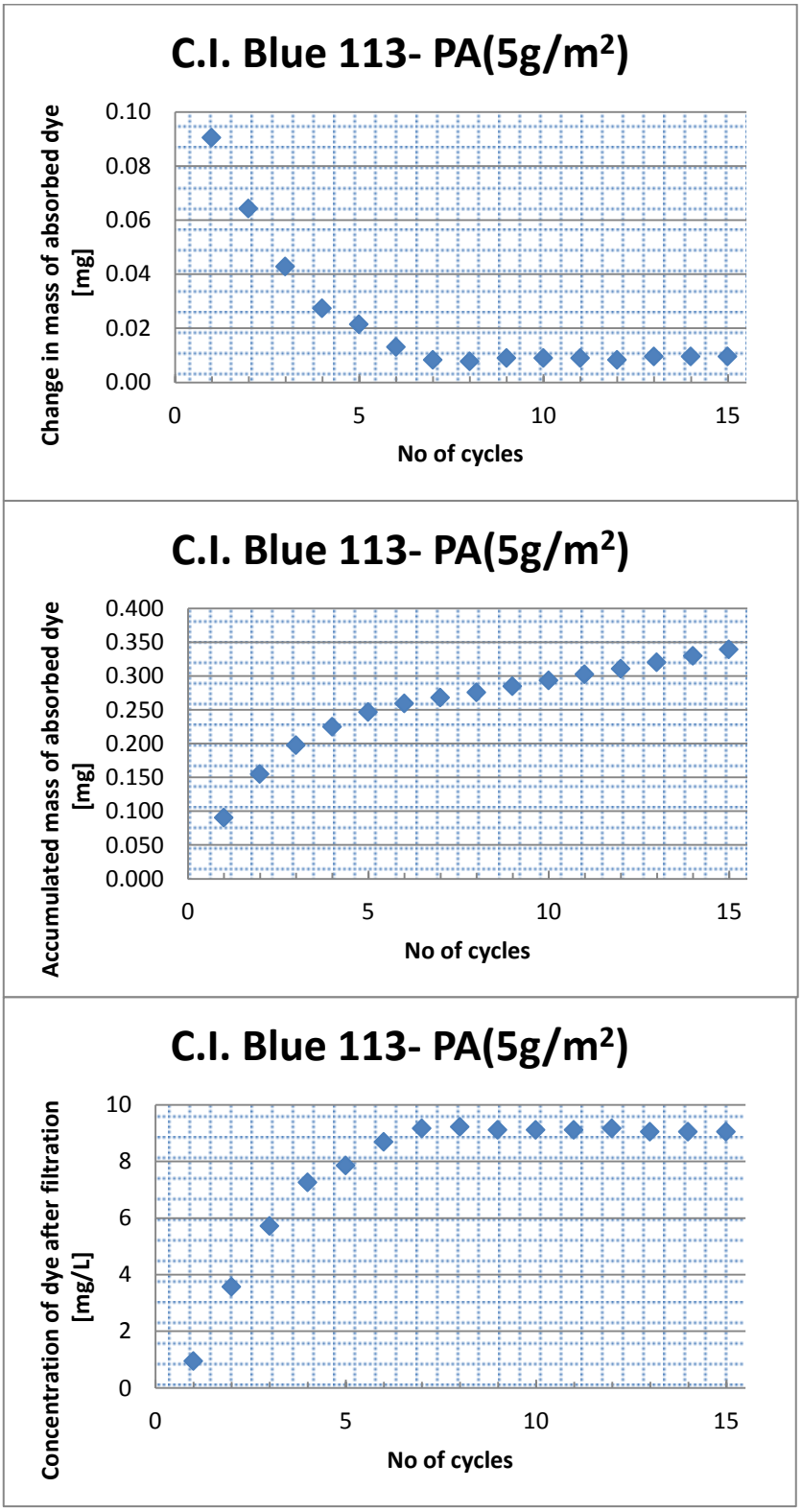


Figure 20 (Combination of graphs drawn using table 8, dyestuff and sorbent material used on top of each graph)

Table 9 (Sorption-filtration experimental results of C.I. Blue 113)

No of cycles	Time of flow [s]	concentration of dye in liquor after filtration [mg/L]	Change in mass of absorbed dye[mg]	accumulated mass of absorbed dye[mg]	Accumulative volume[L]	% of dye removed	% (mass of dye/ mass of fabric)
1	31	0.77	0.09	0.09	0.01	92.3	6.8
2	33	2.44	0.08	0.17	0.02	75.6	12.4
3	34	4.40	0.06	0.22	0.03	56.0	16.6
4	35	5.77	0.04	0.27	0.04	42.3	19.7
5	37	7.26	0.03	0.29	0.05	27.4	21.7
6	38	8.33	0.02	0.31	0.06	16.7	23.0
7	38	8.69	0.01	0.32	0.07	13.1	23.9
8	38	9.17	0.01	0.33	0.08	8.3	24.6
9	38	9.17	0.01	0.34	0.09	8.3	25.2
10	39	8.99	0.01	0.35	0.1	10.1	25.9
11	40	8.93	0.01	0.36	0.11	10.7	26.7
12	41	8.93	0.01	0.37	0.12	10.7	27.5
13	45	8.93	0.01	0.38	0.13	10.7	28.3
14	46	8.93	0.01	0.39	0.14	10.7	29.1
15	47	8.93	0.01	0.40	0.15	10.7	29.9

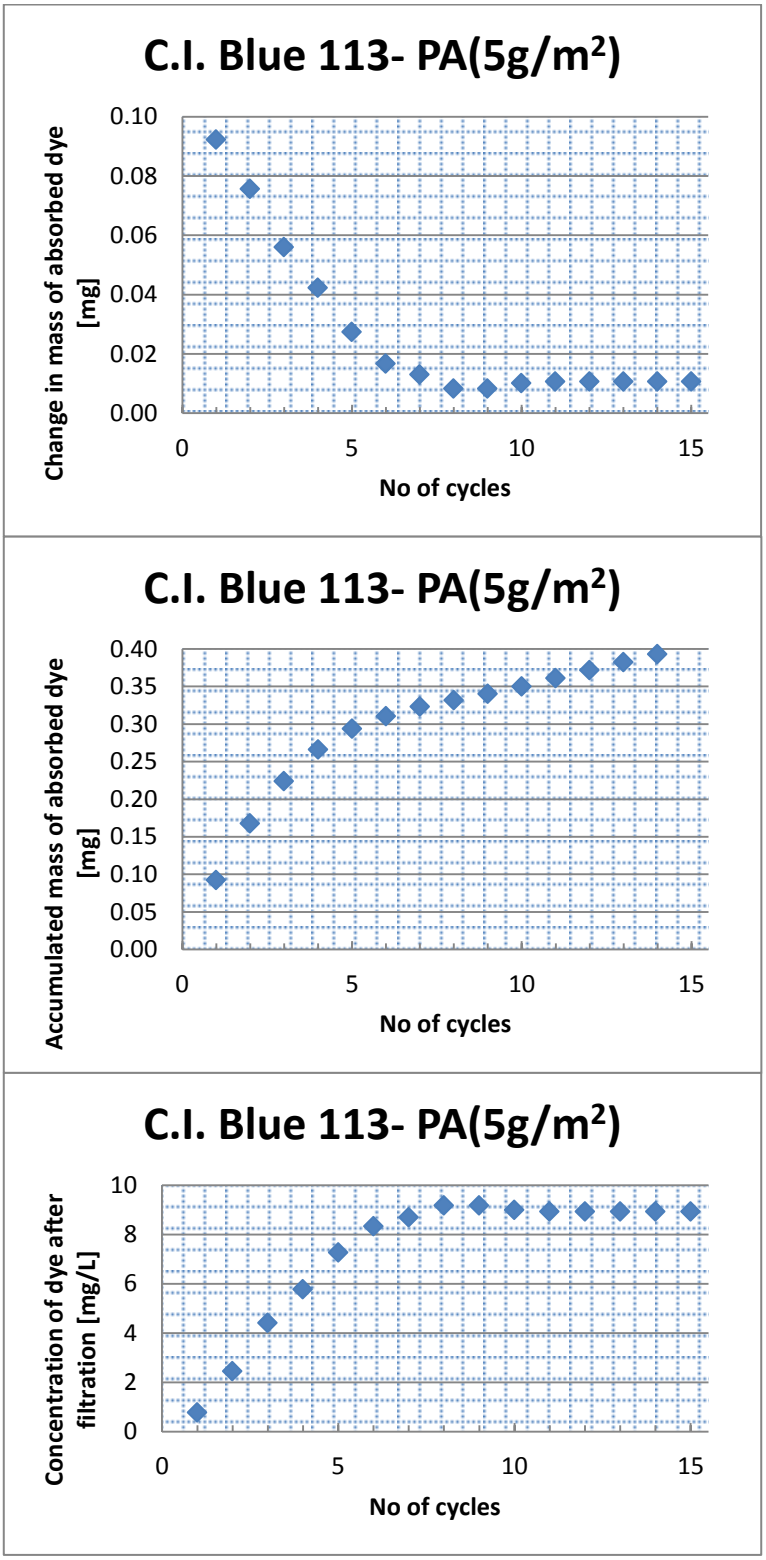


Figure 21 (Combination of graphs drawn using table 9, dyestuff and sorbent material used on top of each graph)

Table 10 (Sorption-filtration experimental results of C.I. Blue 113)

No of cycles	Time of flow [s]	concentration of dye in liquor after filtration [mg/L]	Change in mass of absorbed dye[mg]	accumulated mass of absorbed dye[mg]	Accumulative volume[L]	% of dye removed	% (mass of dye/ mass of fabric)
1	57	19.27	0.81	0.81	0.1	80.7	29.9
2	58	48.97	0.51	1.32	0.2	51.0	48.8
3	58	66.74	0.33	1.65	0.3	33.3	61.1
4	59	76.95	0.23	1.88	0.4	23.1	69.7
5	60	78.10	0.22	2.10	0.5	21.9	77.8
6	62	87.61	0.12	2.22	0.6	12.4	82.4
7	66	87.73	0.12	2.35	0.7	12.3	86.9
8	66	88.19	0.12	2.46	0.8	11.8	91.3
9	69	90.37	0.10	2.56	0.9	9.6	94.8
10	75	93.12	0.07	2.63	1	6.9	97.4

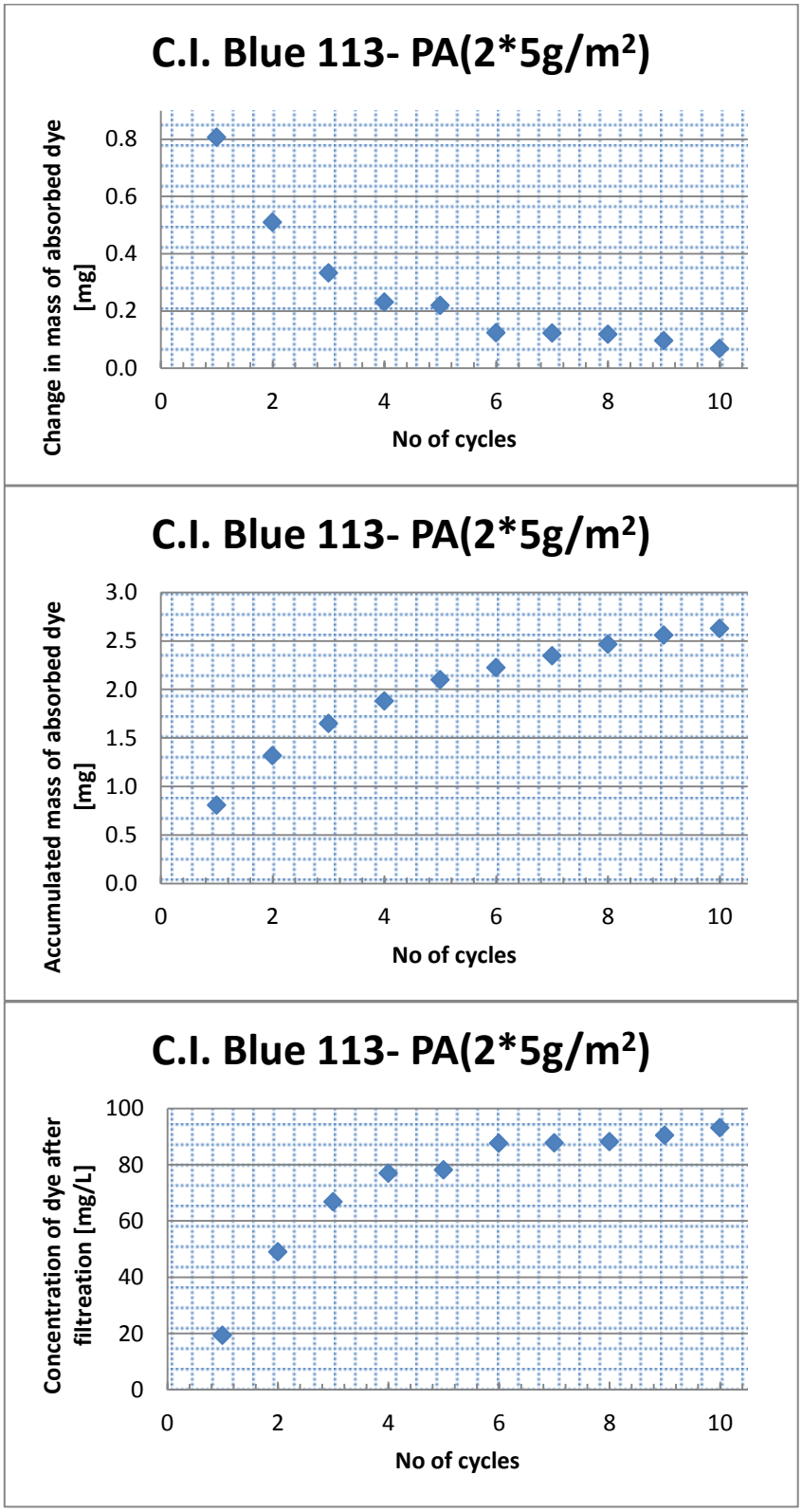


Figure 22 (Higher concentration of 0, 1 g/L was used and double nanolayers were used as filter media)

Table 11 (Sorption-filtration experimental results of C.I.Yellow 40)

No of cycles	Time of flow [s]	concentration of dye in liquor after filtration [mg/L]	Change in mass of absorbed dye[mg]	accumulated mass of absorbed dye[mg]	Accumulative volume[L]	% of dye removed	% (mass of dye/ mass of fabric)
1	21	6.35	0.037	0.037	0.01	36.5	2.7
2	21	8.17	0.018	0.055	0.02	18.3	4.1
3	22	9.27	0.007	0.062	0.03	7.3	4.6
4	23	9.45	0.005	0.068	0.04	5.5	5.0
5	24	9.49	0.005	0.073	0.05	5.1	5.4
6	24	9.80	0.002	0.075	0.06	2.0	5.5
7	25	9.80	0.002	0.077	0.07	2.0	5.7
8	25	9.71	0.003	0.079	0.08	2.9	5.9
9	27	9.77	0.002	0.082	0.09	2.3	6.1
10	27	9.78	0.002	0.084	0.1	2.2	6.2
11	27	9.78	0.002	0.086	0.11	2.2	6.4
12	27	9.78	0.002	0.088	0.12	2.2	6.5
13	28	9.78	0.002	0.091	0.13	2.2	6.7
14	30	9.82	0.002	0.092	0.14	1.8	6.8
15	30	9.82	0.002	0.094	0.15	1.8	7.0
16	30	9.87	0.001	0.096	0.16	1.3	7.1
17	32	9.92	0.001	0.096	0.17	0.8	7.1
18	32	9.87	0.001	0.098	0.18	1.3	7.2
19	32	9.78	0.002	0.100	0.19	2.2	7.4
20	32	9.65	0.004	0.103	0.2	3.5	7.7

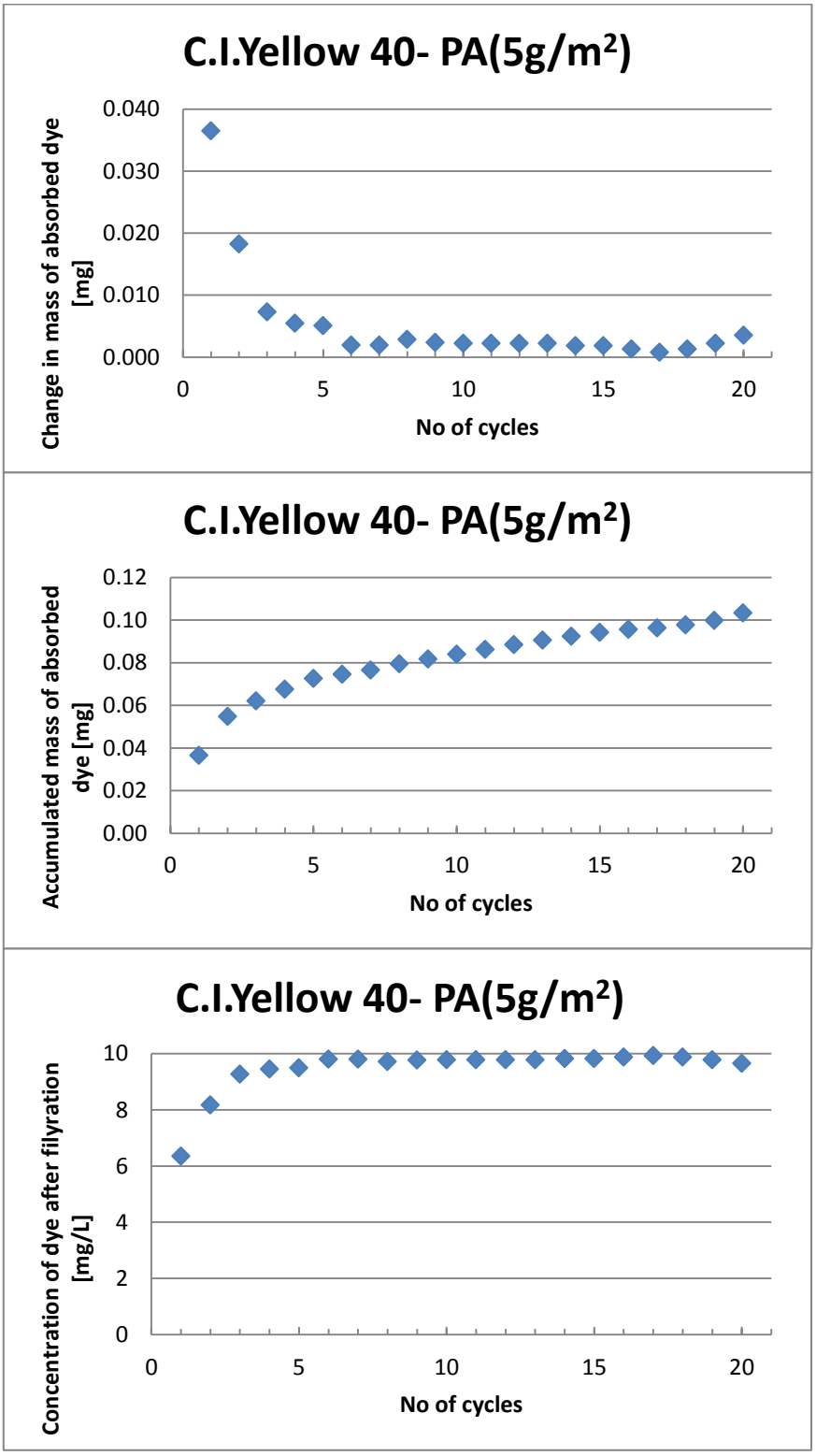


Figure 23 (Combination of graphs drawn using table 11, dyestuff and sorbent material used on top of each graph)

Table 12 (Sorption-filtration experimental results of C.I.Yellow 40)

No of cycles	Time of flow [s]	concentration of dye in liquor after filtration [mg/L]	Change in mass of absorbed dye[mg]	accumulated mass of absorbed dye[mg]	Accumulative volume[L]	% of dye removed	% (mass of dye/ mass of fabric)
1	142	4.01	0.060	0.060	0.01	59.9	2.2
2	993	6.95	0.030	0.090	0.02	30.5	3.3
3	909	8.76	0.012	0.103	0.03	12.4	3.8
4	789	9.24	0.008	0.110	0.04	7.6	4.1
5	724	9.41	0.006	0.116	0.05	5.9	4.3
6	687	9.65	0.004	0.120	0.06	3.5	4.4
7	645	9.84	0.002	0.121	0.07	1.6	4.5
8	640	9.73	0.003	0.124	0.08	2.7	4.6
9	595	9.88	0.001	0.125	0.09	1.2	4.6
10	595	9.65	0.004	0.129	0.1	3.5	4.8

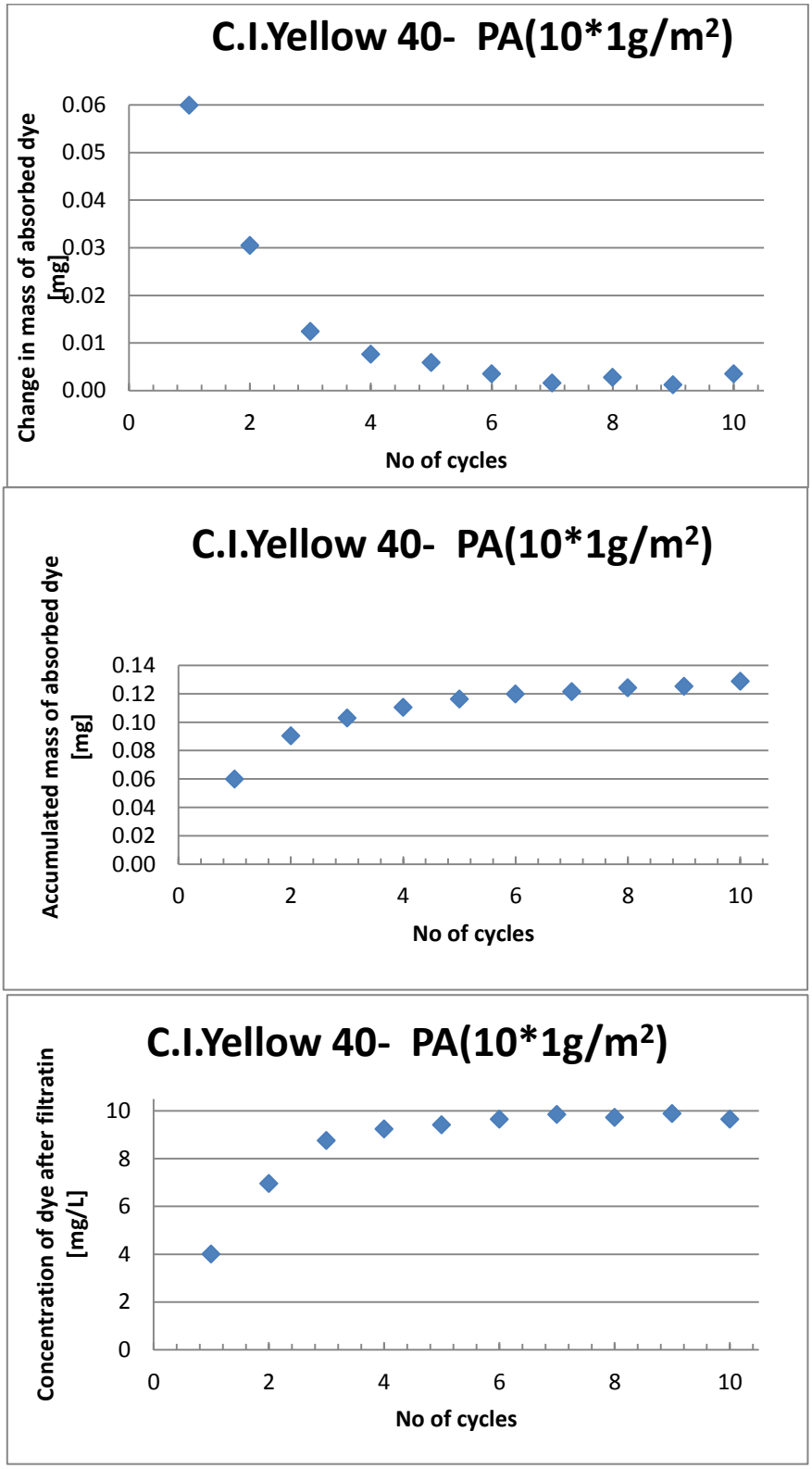


Figure 24 (Combination of graphs drawn using table 12, dyestuff and sorbent material used on top of each graph) this stands for 10*1g/m^2 the number of nanolayers used in this case it 10 layers.

Table 13 (Sorption-filtration experimental results of C.I Red 118)

No of cycles	Time of flow [s]	concentration of dye in liquor after filtration [mg/L]	Change in mass of absorbed dye[mg]	accumulated mass of absorbed dye[mg]	Accumulative volume[L]	% of dye removed	% (mass of dye/ mass of fabric)
1	822	3.35	0.066	0.066	0.01	66.5	2.5
2	678	5.70	0.043	0.109	0.02	43.0	4.1
3	628	7.38	0.026	0.136	0.03	26.2	5.0
4	562	8.30	0.017	0.153	0.04	17.0	5.7
5	510	8.52	0.015	0.167	0.05	14.8	6.2
6	502	9.13	0.009	0.176	0.06	8.7	6.5
7	480	9.15	0.009	0.185	0.07	8.5	6.8
8	451	9.19	0.008	0.193	0.08	8.1	7.1
9	443	9.10	0.009	0.202	0.09	9.0	7.5
10	430	9.13	0.009	0.211	0.1	8.7	7.8

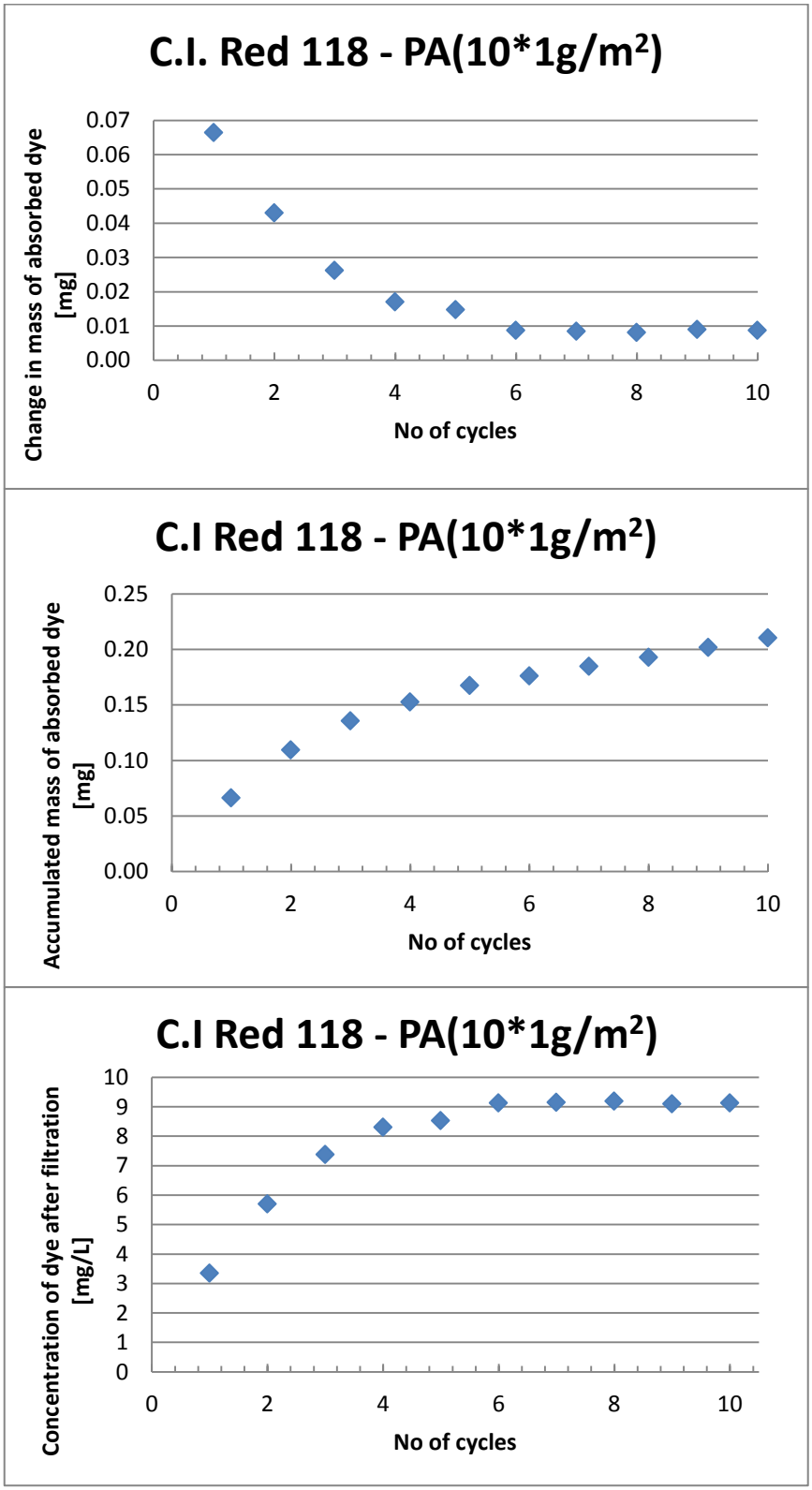


Figure 25 (Combination of graphs drawn using table 13, dyestuff and sorbent material used on top of each graph) this stands for 10*1g/m^2 the number of nanolayers used in this case it 10 layers.

Table 14 (Sorption-filtration experimental results of C.I Red 118)

No of cycles	Time of flow [s]	concentration of dye in liquor after filtration [mg/L]	Change in mass of absorbed dye[mg]	accumulated mass of absorbed dye[mg]	Accumulative volume[L]	% of dye removed	% (mass of dye/ mass of fabric)
1	25	2.62	0.07	0.07	0.01	73.8	5.5
2	27	5.66	0.04	0.12	0.02	43.4	8.7
3	27	6.46	0.04	0.15	0.03	35.4	11.3
4	28	7.59	0.02	0.18	0.04	24.1	13.1
5	27	8.00	0.02	0.20	0.05	20.0	14.6
6	27	8.61	0.01	0.21	0.06	13.9	15.6
7	27	8.69	0.01	0.22	0.07	13.1	16.6
8	27	8.80	0.01	0.24	0.08	12.0	17.5
9	27	9.20	0.01	0.24	0.09	8.0	18.1
10	27	8.80	0.01	0.26	0.1	12.0	18.9
11	28	8.70	0.01	0.27	0.11	13.0	19.9
12	27	9.31	0.01	0.28	0.12	6.9	20.4
13	27	9.07	0.01	0.28	0.13	9.3	21.1
14	27	9.26	0.01	0.29	0.14	7.4	21.7
15	26	8.66	0.01	0.31	0.15	13.4	22.6
16	26	9.49	0.01	0.31	0.16	5.1	23.0
17	28	9.44	0.01	0.32	0.17	5.6	23.4

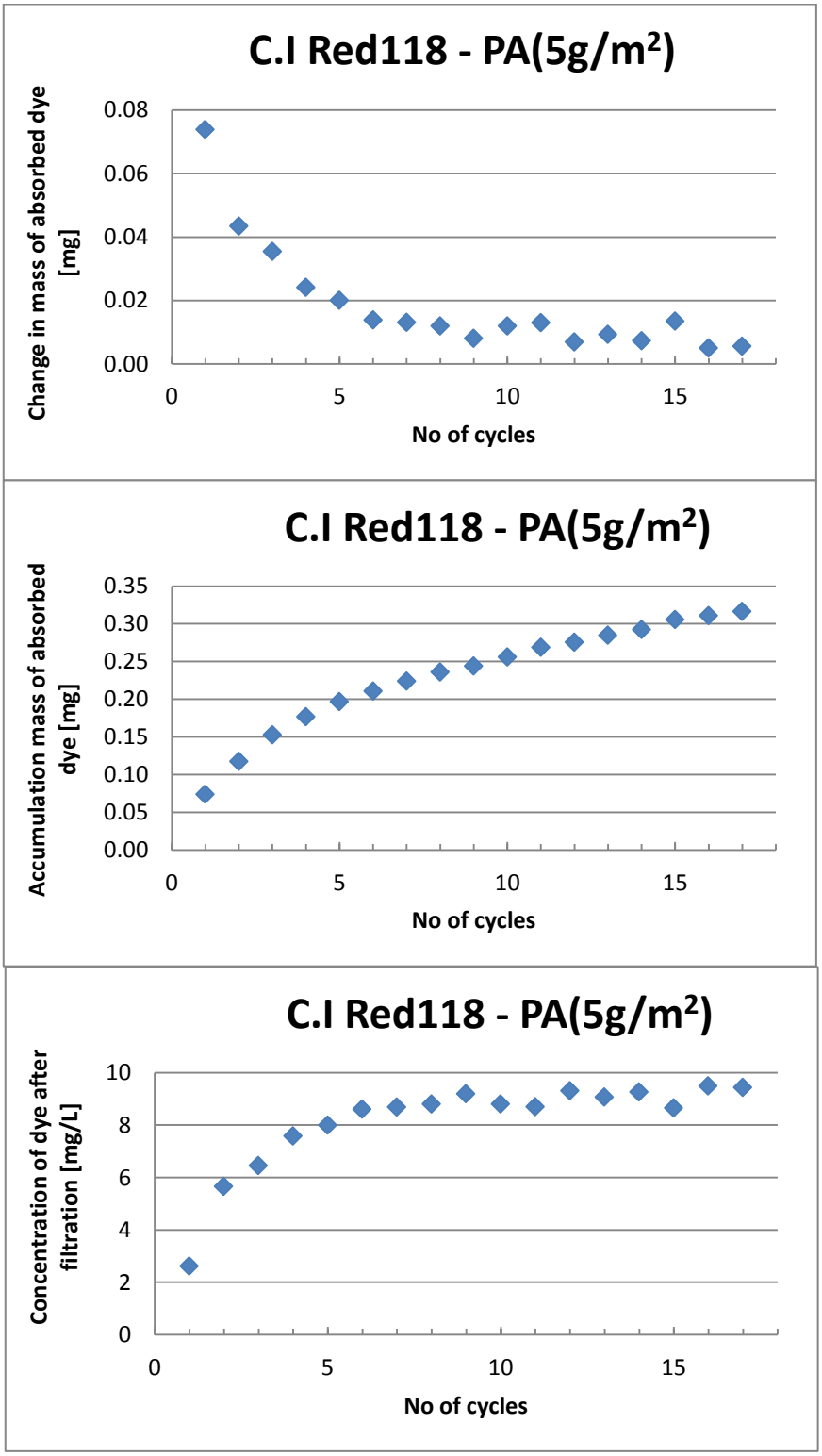


Figure 26 (Combination of graphs drawn using table 14, dyestuff and sorbent material used on top of each graph)

Table 15 (Sorption-filtration experimental results of C.I Blue 41)

No of cycles	Time of flow [s]	concentration of dye in liquor after filtration [mg/L]	Change in mass of absorbed dye[mg]	accumulated mass of absorbed dye[mg]	Accumulative volume[L]	% of dye removed	% (mass of dye/ mass of fabric)
1	1131	4.12	0.059	0.059	0.01	58.8	2.2
2	841	7.63	0.024	0.082	0.02	23.7	3.1
3	799	8.82	0.012	0.094	0.03	11.8	3.5
4	737	9.33	0.007	0.101	0.04	6.7	3.7
5	699	9.27	0.007	0.108	0.05	7.3	4.0
6	702	9.57	0.004	0.113	0.06	4.3	4.2
7	657	9.55	0.005	0.117	0.07	4.5	4.3
8	625	9.59	0.004	0.121	0.08	4.1	4.5
9	615	9.66	0.003	0.125	0.09	3.4	4.6
10	585	9.80	0.002	0.127	0.1	2.0	4.7

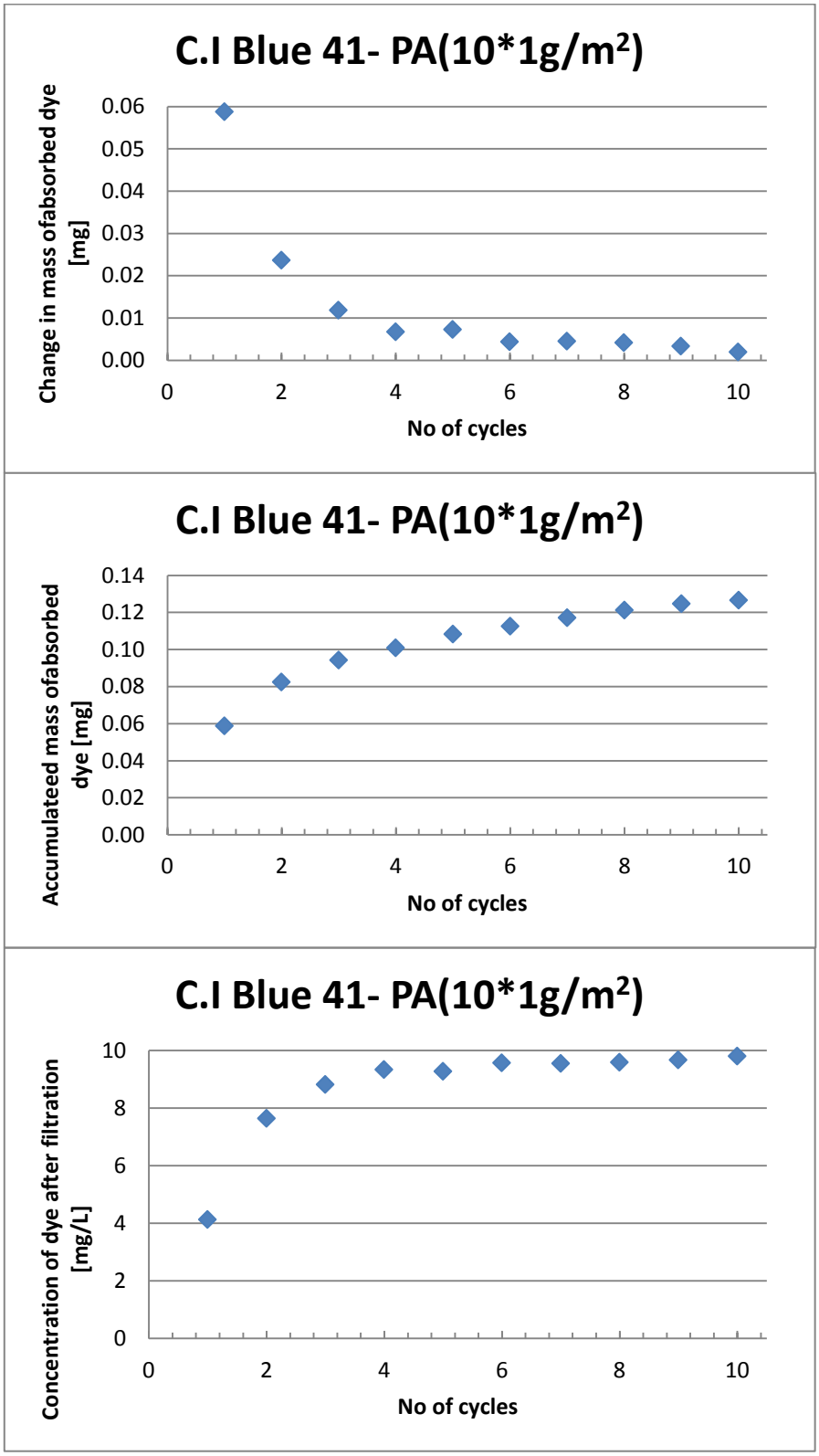


Figure 27 (Combination of graphs drawn using table 15, dyestuff and sorbent material used on top of each graph) this stands for 10*1g/m^2 the number of nanolayers used in this case it 10 layers.

Table 16 (Sorption-filtration experimental results of C.I Blue 41)

No of cycles	Time of flow [s]	concentration of dye in liquor after filtration[m/L]	Change in mass of absorbed dye[mg]	accumulated mass of absorbed dye[mg]	Accumulative volume[L]	% of dye removed	% (mass of dye/ mass of fabric)
1	18	3.976	0.060	0.060	0.01	60.2	1.9
2	18	7.317	0.027	0.087	0.02	26.8	2.7
3	18	8.293	0.017	0.104	0.03	17.1	3.2
4	18	8.878	0.011	0.115	0.04	11.2	3.6
5	18	9.268	0.007	0.123	0.05	7.3	3.8
6	18	9.439	0.006	0.128	0.06	5.6	4.0
7	18	9.537	0.005	0.133	0.07	4.6	4.1
8	18	9.537	0.005	0.138	0.08	4.6	4.3
9	18	9.659	0.003	0.141	0.09	3.4	4.4
10	18	9.829	0.002	0.143	0.1	1.7	4.4
11	18	9.756	0.002	0.145	0.11	2.4	4.5
12	18	10.000	0.000	0.145	0.12	0.0	4.5
13	18	10.146	-0.001	0.144	0.13	-1.5	4.4
14	18	10.000	0.000	0.144	0.14	0.0	4.4
15	18	10.000	0.000	0.144	0.15	0.0	4.4
16	18	10.000	0.000	0.144	0.16	0.0	4.4
17	18	10.000	0.000	0.144	0.17	0.0	4.4
18	18	10.000	0.000	0.144	0.18	0.0	4.4
19	18	10.000	0.000	0.144	0.19	0.0	4.4
20	18	10.171	-0.002	0.142	0.2	-1.7	4.4

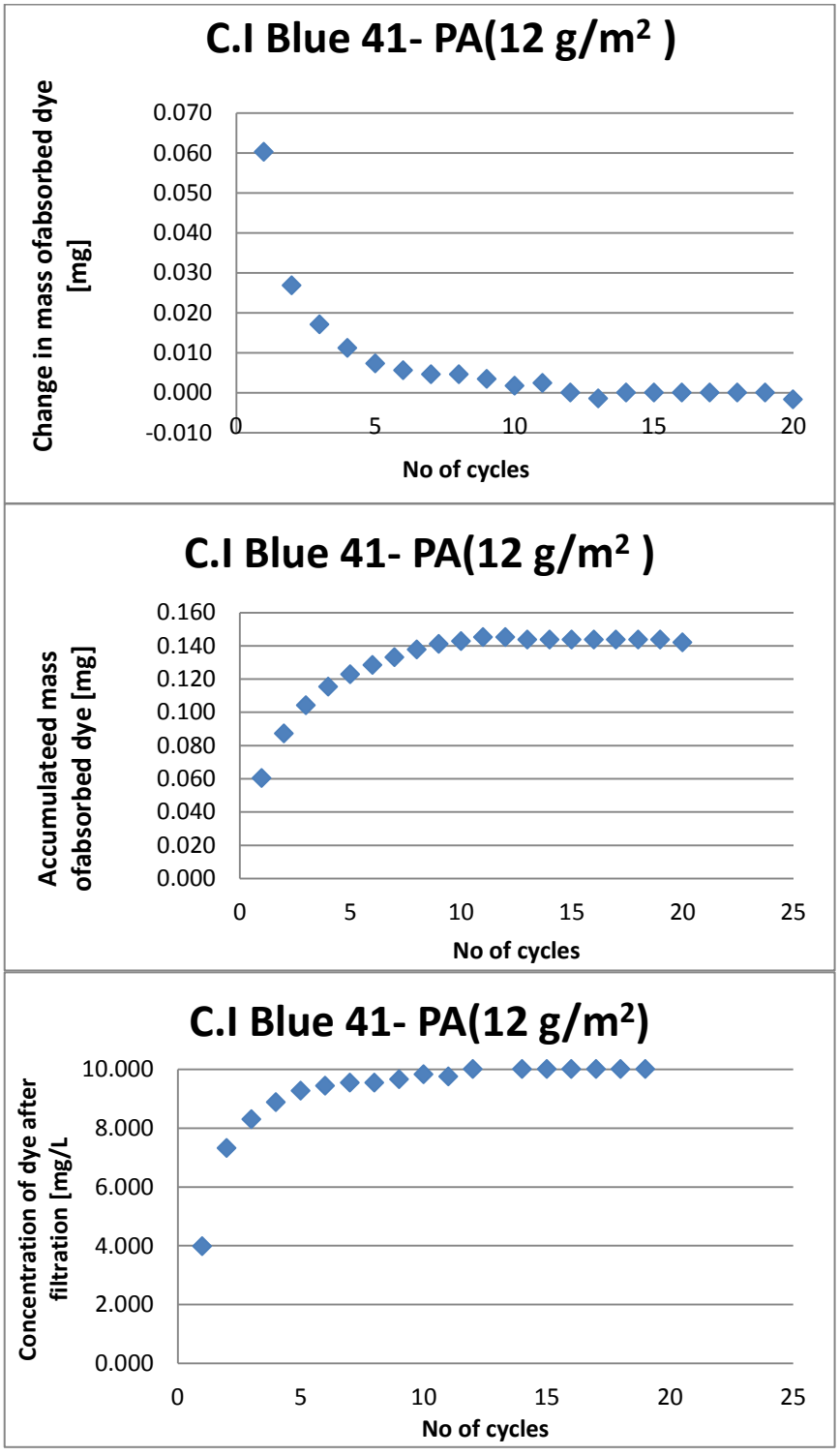


Figure 28 (Combination of graphs drawn using table 16, dyestuff and sorbent material used on top of each graph)

3.6.2 Discussion of sorption filtration result

There was high removal percentage on C.I. Blue 113 dyestuff when compared with other acid dyes. It was also observed that even on higher concentration (Figure 22 and Table 10) the removal percentage was not less than 80% when double nanolayers of nanofibers were used. The duration of each cycle was very short in single nanolayers around about 45 seconds as the maximum when compared to more number of nanolayers, which also indicated that when the numbers of layers were increased the percentage removal was increased (Figure 24, 25 and Table 12, 13). The difference in percentage removal when all dyestuffs were compare it was concluded that it can be related to the molecular structure of dye because the dyes were observed in the same concentration however some were very faith at this concentration10mg/L.

With sorption-filtration method the removal of colour from simulated wastewater concentration was possible at shorter time and the apparatus used were able to protect the nanofiber filter from mechanical damage as it was supported by the filter supporting unit. The equilibrium result obtained can be theoretical related to Langmuir assumptions that states once the site of substrate are filled with dye particles ,the site can be taken as saturated meaning no further absorption can occur and this can be viewed in all sorption experiments that after the 10^{th} cycle the equilibrium point was reached. $\boldsymbol{No.of\ cycles * time\ of\ each\ cycle}$ Can be used to relate this with equilibrium isotherms for future evaluation of results.

4 Conclusion

The first and the second part of the presented study were based on the comparison of two textile substrates from polyamide 6, one was standard fibers and the second one was nanofibers. The sorption properties of both substrates were tested. The C.I. Blue 113 was used as the sorbate. The kinetics of sorption was analyzed by diffusion model and Cegarra-Puente equation. Where equilibrium experiments of sorption were best described by Langmuir isotherm.

The calculated value of diffusion coefficient for nanofibers was very small when compared to the standard fibers approximately 3547 times lower. There was no easy explanation as to why the difference was so huge. However the possible hypothesis was that since all experiments were performed at low temperature +/- 22 ^{o}C which can be considered to be low for sorption of dyestuff molecules to the solid polyamide 6 polymer and with this it can be said that the dyestuff was absorbed on the surface of the (macroscopic surface of fibre and also the surface of internal pores in the mass of fibres). The polymer surface was much higher in nanofibers based on the equilibrium concentration, however the size of internal pores in the polymer mass was probably smaller. To further illustrate on the small pore size on nanofibers it can be explained by the low rate of diffusion, because the dye molecules would all the time be in contact with the surface of pores by sorption forces.

The presented hypothesis was supported by equilibrium of sorption which was estimated by a period of 10 days for sorption equilibrium experiments. The equilibrium of sorption experiments was best described by Langmuir isotherm, where Langmuir saturation constant S and Langmuir K constant were calculated. The constant parameter K of Langmuir was approximately the same on both nanofibers and standard fibers, whereas the Langmuir saturation constant S was approximately 10 times higher in nanofibers compared to standard fibers. The saturation difference can be explained again by the difference in surface area of fibres, it can be concluded that nanofibers high surface area makes it possible to absorb more constituents than standard conventional sorbents.

In filtration-sorption there was high removal percentage on C.I. Blue 113 dyestuff when compared with other acid dyes. It was also observed that even on higher concentration (Figure 22 and Table 10) the removal percentage was not less than 80% when double nanolayers of nanofibers were used. The duration of each cycle was very short in single nanolayers around about 45 seconds as the maximum whereas the duration time of each cycle was increasing if the number of layers were increased, which also indicated that when the numbers of layers were increased the percentage removal also increased. The difference in percentage removal when all dyestuffs were compare it was concluded that it can be related to the molecular structure of dye since all the dyes were observed in the same concentration however some were very faith 10mg/L.

With this method the removal of colour from simulated wastewater concentration was possible at shorter time and the instruments used were able to protect the nanofiber filter from mechanical damage as it was supported by the filter supporting unit. The equilibrium result obtained can be theoretical related to Langmuir assumptions that states once the site of substrate are filled with dye particles ,the site can be taken as saturated meaning no further absorption can occur and this can be viewed in all sorption experiments that after the 10^{th} cycle the equilibrium point was reached.

To further test the ability of used sorbent material in this study, especially in filtration sorption process different types of dyes can be used, concentration and volume solution size on different sorbents can also be used. Temperature and pH can also be other factors to look at if the real wastewater from textile industry can be used in this method.

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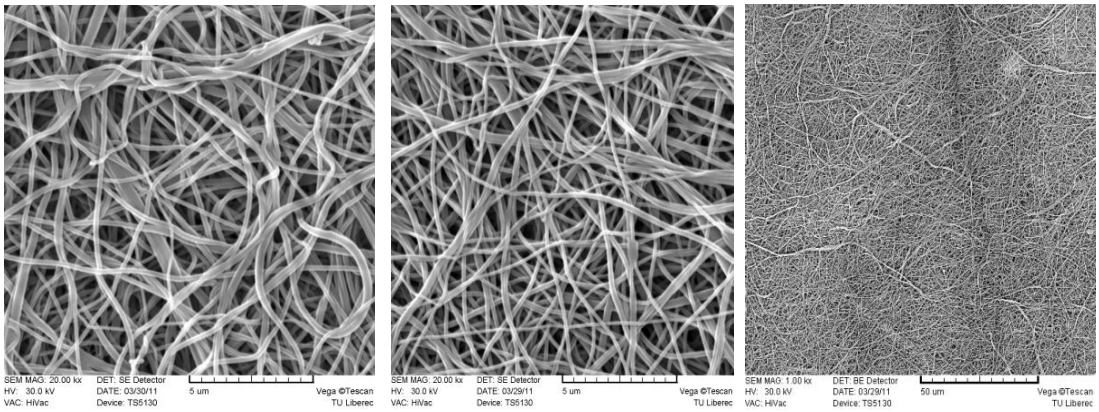
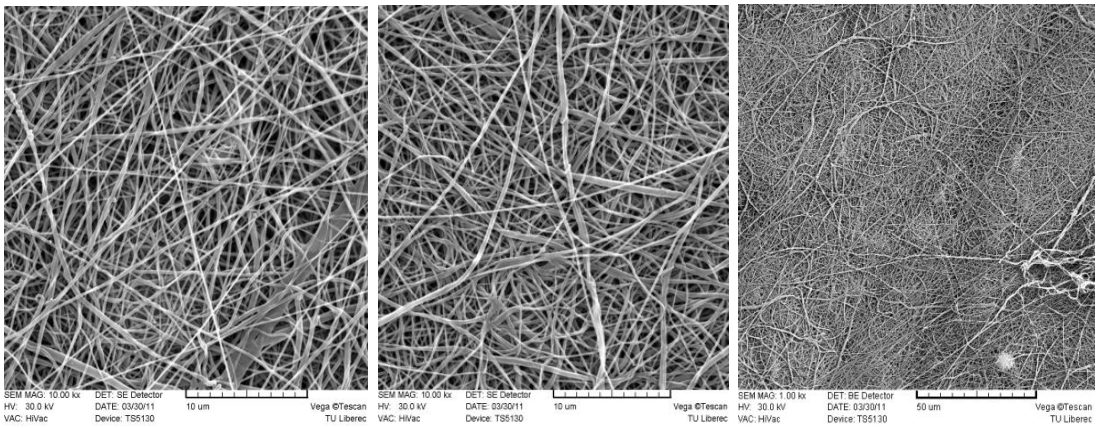
Appendix

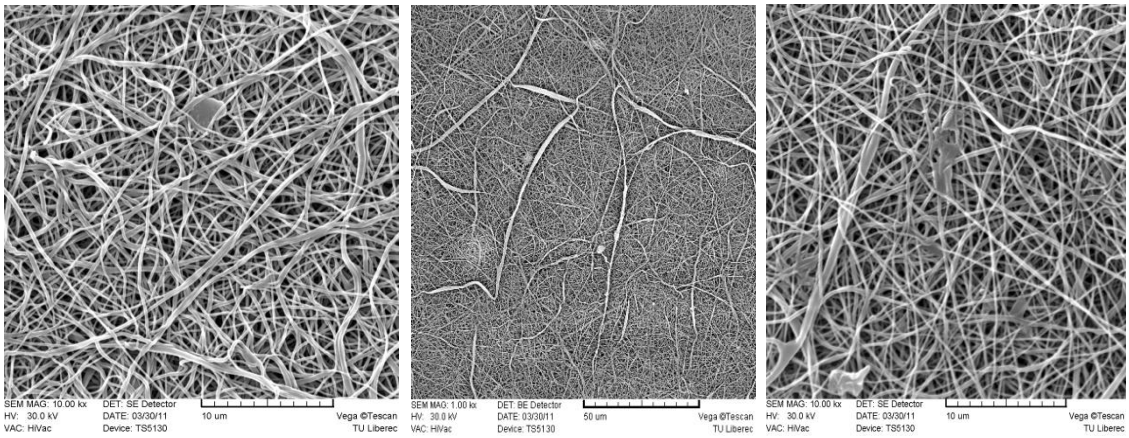
C.I. Blue 41before filtration-sorption



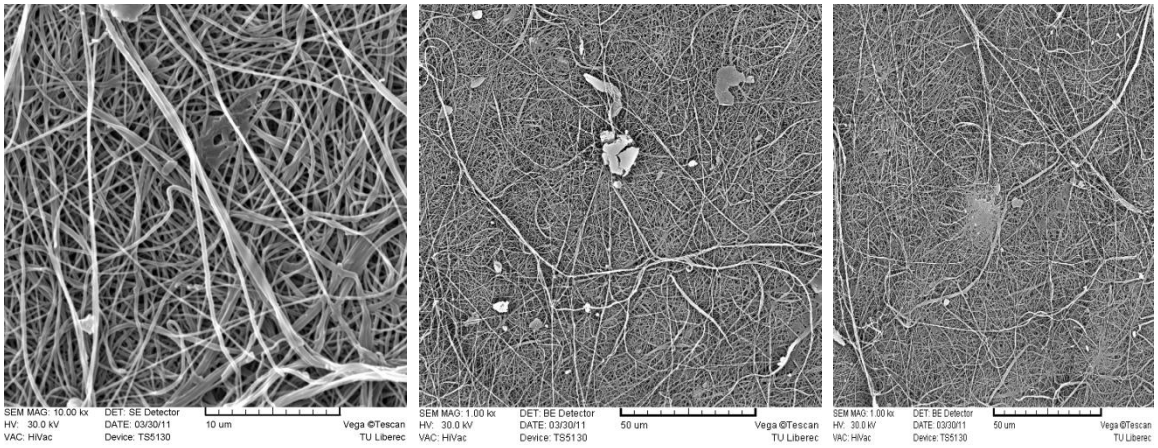
C.I. Blue 41 after filtration sorption



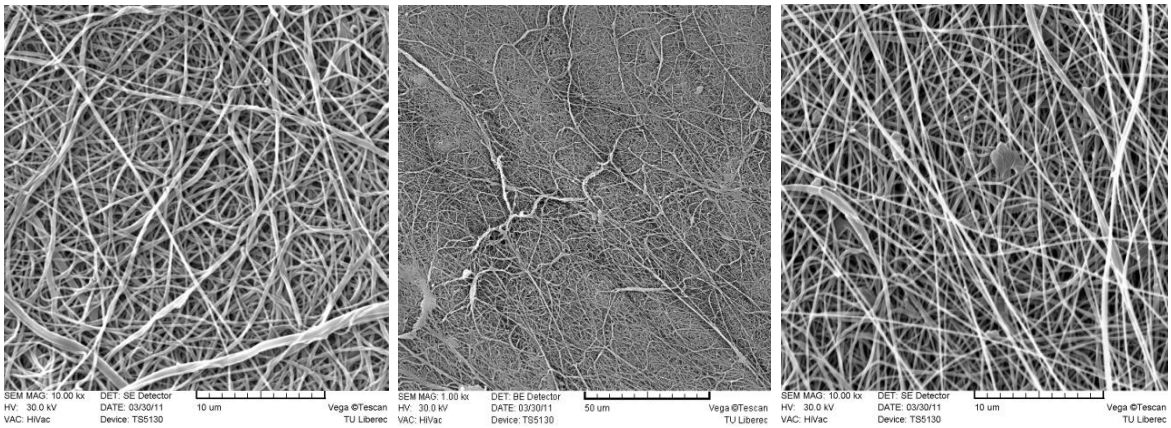
C.I. Red 118 before



C.I. Red 118 After



C.I. Yellow 40 Before



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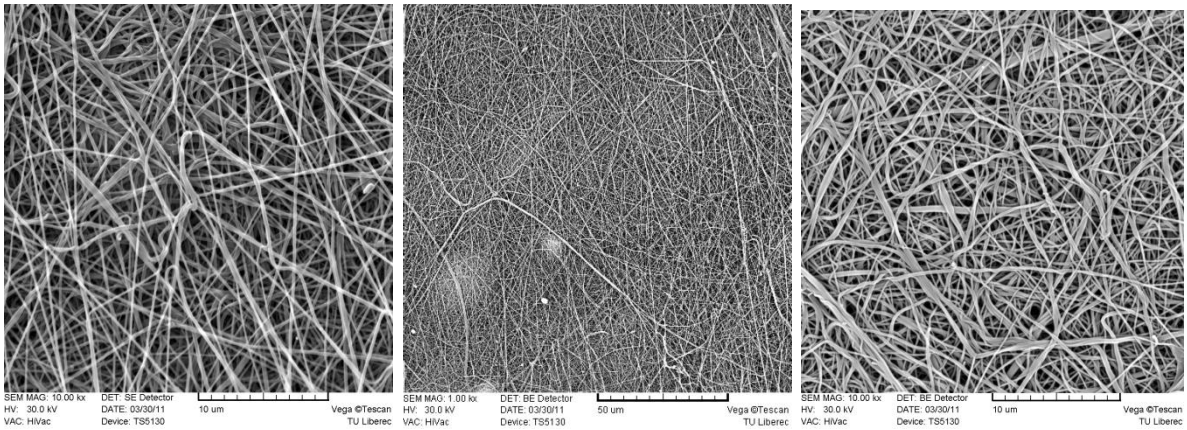
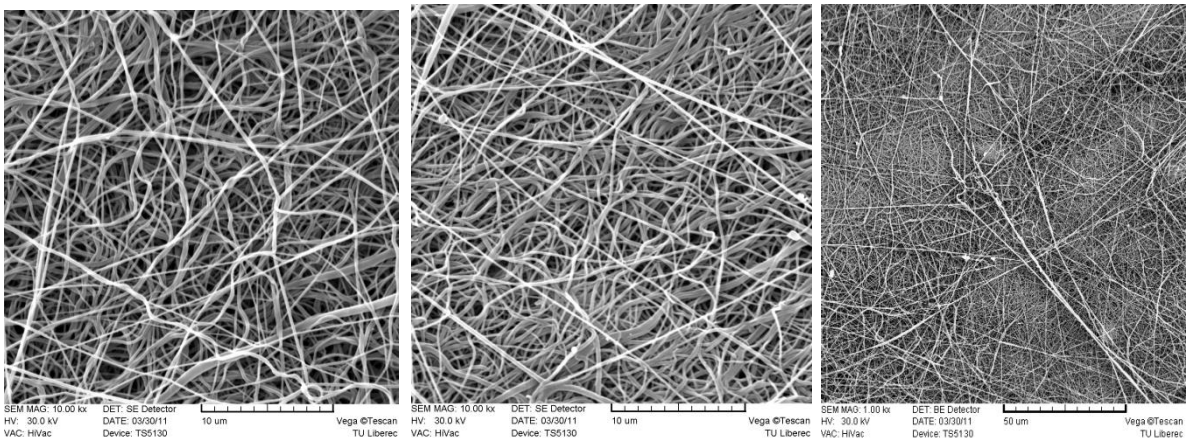


C.I. Blue 113 Before



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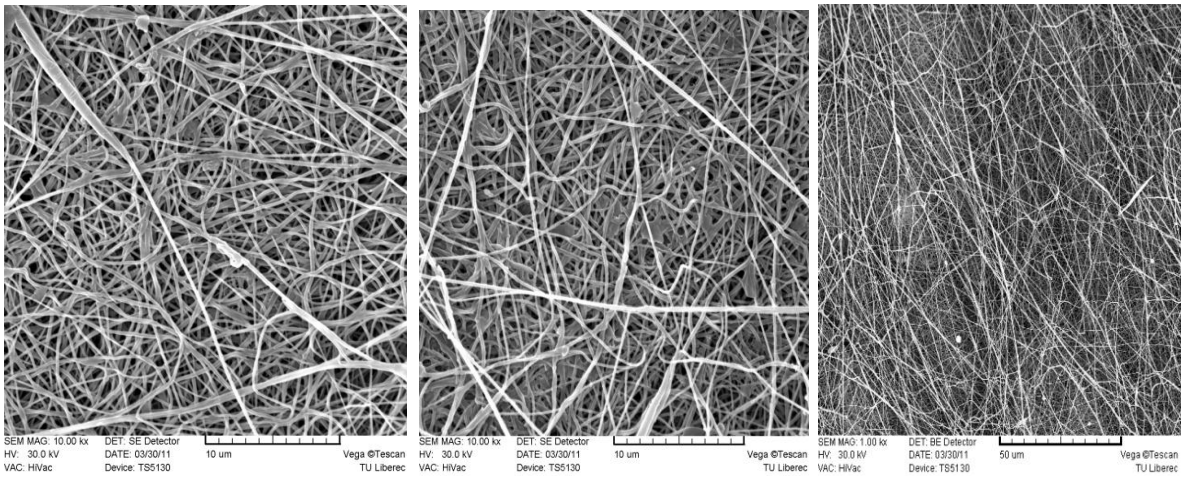

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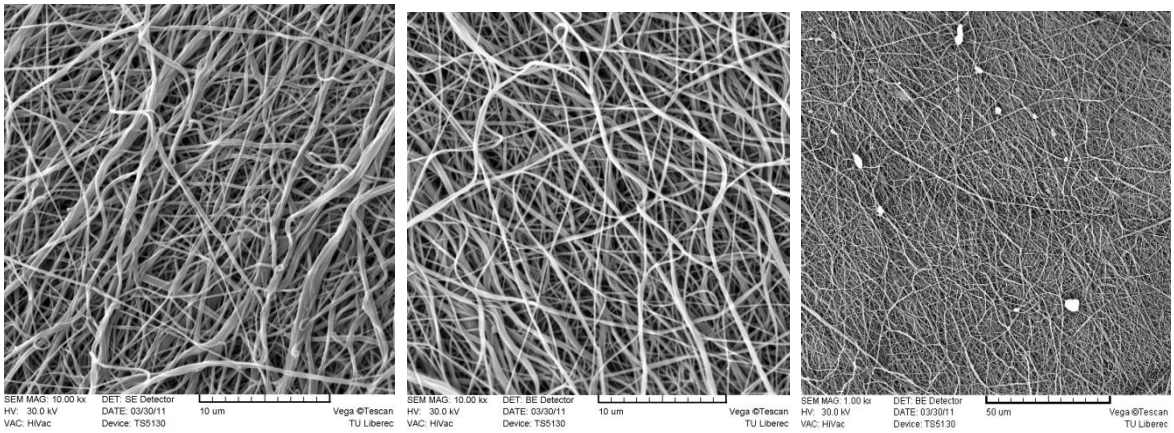

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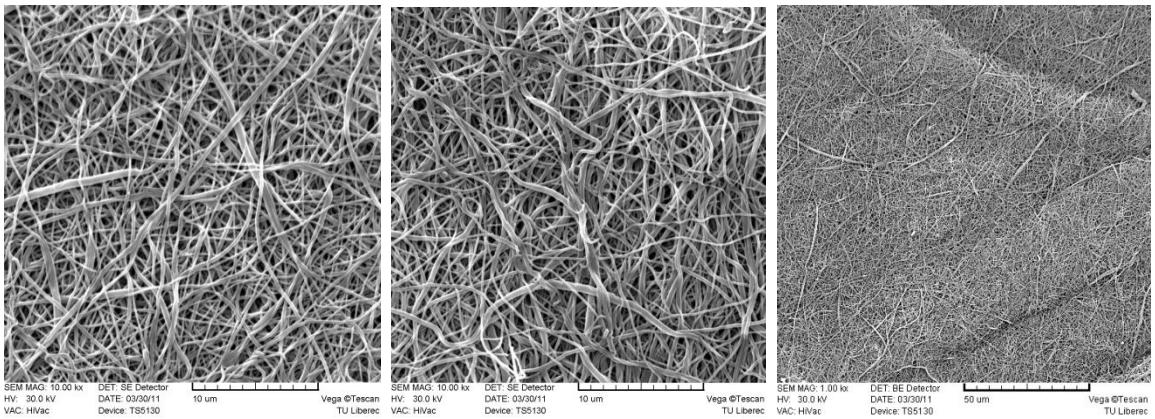
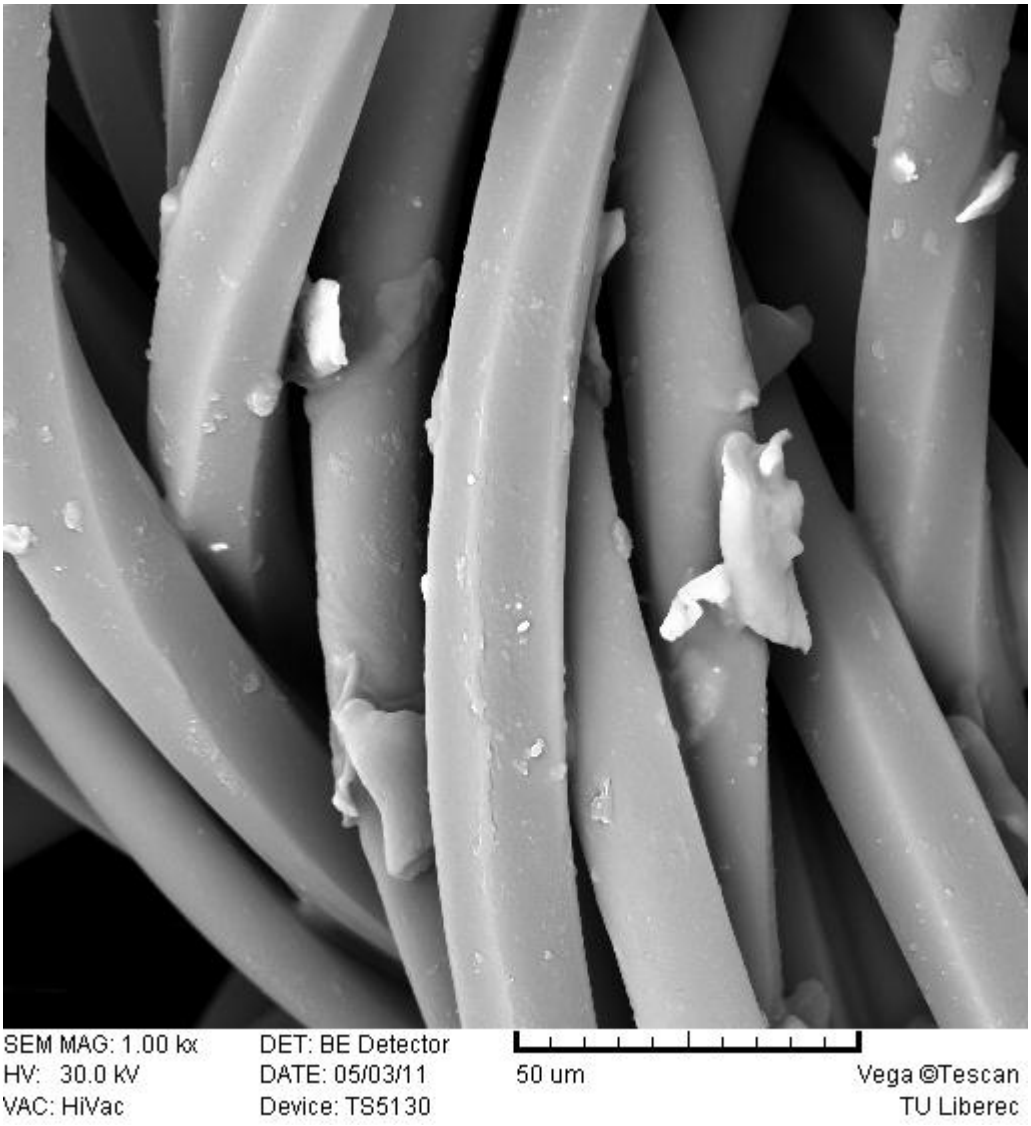
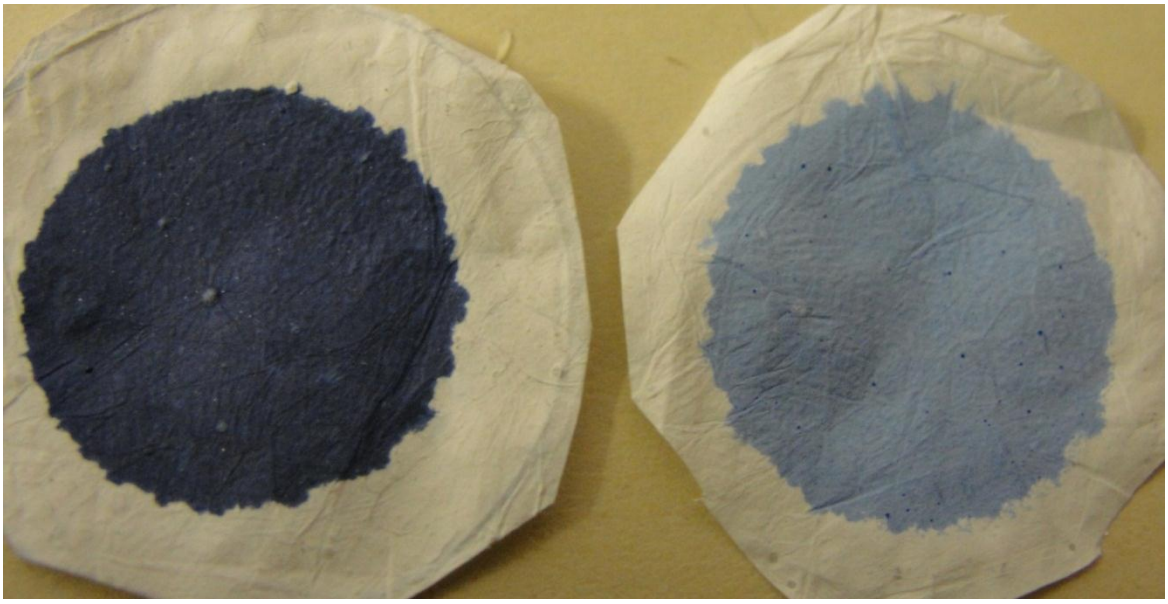


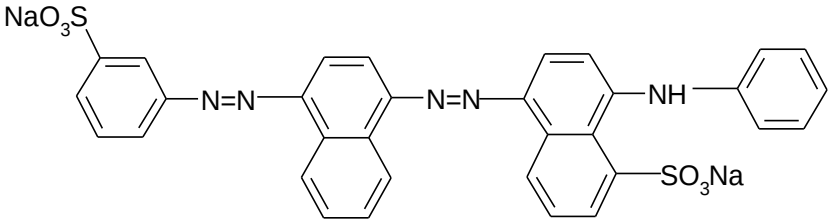


Polyamide 6 standard fibers

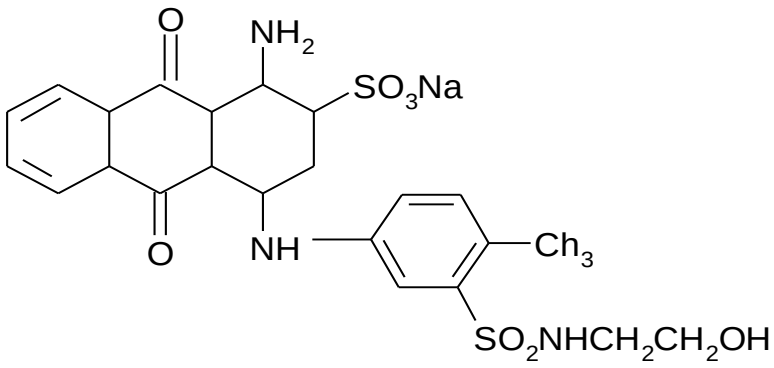


Left represents C.I. Blue 113 *and right C.I. Blue 41*

Chemical structure of used dyes



C.I. Blue 113



C.I. Blue 41 acid dyes